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Studies in Industrial Crystallisation.

A thesis submitted to Glasgow University in fulfilment of the requirements of the Degree of Doctor of Philosophy.

by

John Bain.

The Royal College of Science and Technology, Glasgow.

April, 1960.

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A C K N O W L E D G E M E N T S

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P U B L I C A T I O N S

The bulk of the work on sodium chloride crystallisation was summarised in a paper presented to the Institution of Chemical Engineers (London Section) in October, 1959.

(Bain and Rumford, Trans. Instn. Chem. Engs., 1960, 38, 10).

A note has been published in Chemistry and Industry: "A spring flowmeter for saturated salt solutions."

(Bain and Porter, Chem. and Ind., 1960, February, p.225).

Summary.

An investigation was made of the crystallising properties of sodium chloride, sodium thiosulphate α-pentahydrate, and barium hydroxide octahydrate, in fluidised bed crystallisers. The operational proceedure was either to grow batches of crystals under known degree of supersaturation to determine rate of growth, or to grow crystals continuously to determine crystal size and quality.

It was found that the diffusive presentation of solute to the crystal surface was, in general, slower than the rate of surface reaction. This was probably caused by the low relative velocity of crystal and solution in fluidised bed crystallisation, and by the imperfections in structure produced by the collisions in the fluidised bed. Typical mass transfer coefficients are 80, 4, and 50 gms./cm.^{2} x hr. x gm./c.c. for the three solutes, in the order given above.

The crystals showed a resistance to growth below supersaturations of the order of 0.5 gms./litre, which agrees with the work of Burton and Cabrera, (Disc. of the Far. Soc., No.5, "Crystal Growth", 1949) who showed that a lower metastable limit for growth is possible.

The effect of temperature on growth rate was

found to vary with the solute. Sodium chloride growth rate increased with temperature, while sodium thiosulphate pentahydrate and barium hydroxide octahydrate growth rates remained almost constant with temperature increase.

Under production conditions in the crystalliser, at some specific working temperature, the metastable limits for bulk nucleation are 1.6, 50, and 2.8 gms./litre, (supersaturation coefficients of 1.005, 1.048, and 1.025) for the three solutes. Just before supersaturation reaches the metastable limit the crystals become covered with protruberances which probably signify dendritic growth, and poor crystal structure.

The measured rates of crystal growth showed an adequate degree of repeatability, and it was possible to scale up results from a one inch diameter batch cooling crystalliser up to a one foot diameter continuous evaporative crystalliser.

The product crystal for each solute was greater than 16 mesh under continuous production conditions, with no dust present. The crystals were hard, tended to be spherical, and had a good lustre. Production rates of 2 m.m. crystals were of the order of 40 lbs/hr. x ft.^{2} of crystalliser cross-sectional area, provided a suitable height of fluidised bed was available.

CONTENTS

A. Introduction.

1. The Process of Industrial Crystallisation.

(a) Commercial importance.

The industrial importance of crystallisation lies in the fact that a crystal produced from a crude solution may be itself very pure. Also, the crystals obtained are in a very suitable form for handling, transport, and storage.

The size and appearance of the crystals are as important commercially as the crystal purity. A product of large, uniformly sized crystals, with a good lustre, will sell more readily than a badly agglomerated product containing a wide range of crystal sizes, and there will be no dust problem. From the producer's point of view a uniformly sized product is superior because it is more easily washed, filtered, and dried, and will contain a smaller amount of occluded mother liquor.

The larger the crystal size, the smaller becomes the surface area per unit mass of crystal, with the result that there is less chance of caking on storage. This is very important, since a sack of small, uneven sized crystals can set into a concrete like mass under humid conditions.

(b) Industrial crystallisers.

The simplest type of crystalliser is the tank crystalliser, where the solution is allowed to evaporate

slowly, as in salt pans, or where hot saturated solution is allowed to cool slowly to the ambient temperature. The stagnant solution gives low heat and mass transfer, and a tank crystalliser has a low production capacity; the labour costs are high; and a large irregular crystal is obtained which is impure by occlusion.

The direct development of the tank crystalliser is the Wulff-Bock crystalliser. A hot saturated solution is cooled by natural convection, but the crystalliser is rocked from side to side, giving better mass transfer. The capacity is low, but a large uniform grain is obtained.

Agitated batch crystallisers and Swenson-Walker crystallisers have water cooled heat exchange surfaces, and are agitated to increase mass and heat transfer. The capacity is higher than that of the previous units, and the grain fairly uniform in size.

Crystallising evaporators give very high production rates, and are normally very efficient heat transfer units with little control over crystal size, although by control of magma density and use of forced circulation large crystals can be produced.[1] A very important exception is the sugar boiling pan, which is operated on a batch basis. The emphasis in sugar

crystallisation is on uniformity and quality of grain rather than high production rates.

The Krystal, or Oslo process of crystallisation was invented by F. Jeremiassen in 1930, and was designed to give controlled crystallisation together with high production rates. The product is characterised by the remarkable uniformity of size, and the tendency for the crystals to be rounded.

The process is continuous, and control is obtained by supersaturating the liquor in one section, and depositing the excess solute on a "fluidised" bed of crystals in another part of the apparatus. Thus the apparatus may be split into two parts, a heat transfer section which may be designed according to the laws of heat transfer, and a mass transfer section which takes advantage of the rapid mass transfer in fluidised beds. The supersaturation may be produced by cooling, evaporation, or "vacuum cooling".

An advantage of the classified fluidised bed is that only fully grown crystals should be taken from the lower levels, the smaller crystals being suspended at the top of the bed. The crystalliser may also be operated with a "rotating mixed bed", as in crystallising evaporators, in which case a less uniform product is obtained.

(c) The design of industrial crystallisers.

Before a crystallisation plant can be designed the chemical engineer must have knowledge of the following physical data for the solute to be crystallised.

The temperature-solubility relationship of the solute.

The temperature-solubility relationship and the heat of crystallisation are essential in order that mass and heat balances may be prepared. An Oslo crystalliser may be considered as a constant volume reactor whose operating conditions are governed by the crystallisation process, and the feed, product, and waste flows are calculated from the above relationships to give the desired production rate.

The rate of growth of the solute crystals.

Each solute has a specific rate of growth which may be expressed as a mass transfer coefficient. The mass transfer coefficient is used to calculate (1) the surface area required to remove the supersaturation from the solution, and hence the mass of crystals which must always be retained in the crystalliser; and (2) the linear increase in size of the crystals per hour, and hence the retention time in the crystalliser to give the desired product size.

The rate of growth is affected by the degree of supersaturation, the temperature, solution purity,

and the relative turbulence of crystals and solution in the crystalliser. Crystal quality is a function of the rate of growth. Too high growth rates can give badly formed crystals,[2] or crystals with large occlusions[3] of mother liquor, and the maximum permissable growth rate which will give good quality crystals must be found experimentally.

The metastable limit of the solute.

If there is insufficient crystal surface area present in the crystalliser then the supersaturation will increase, until either the growth rate of the crystals is sufficiently large to absorb the solute, or until new solute crystals start to form. In an industrial crystalliser new crystals are continually formed because of local concentration fluctuations, crystal attrition, etc., but once a supersaturation characteristic of the solute is reached then nucleation rates become very high and uncontrolled. This limiting concentration is known as the metastable limit, and in order to obtain large uniform crystals, industrial crystallisation should take place in the region between the solubility concentration and the metastable limit.

Product crystal size.

The size of the product crystal is dependent on two main factors. Firstly, the greater the

nucleation rate the smaller the product crystals will be, and secondly, the greater the crystal retention time the larger the crystals will be. The size of the product crystals will be governed by the natural nucleation rate of the crystalliser, unless a fraction of the nuclei are removed.

2. Nucleation.

(a) Solubility and supersolubility in aqueous solution.

The degree of solubility of substances in water varies widely from substances such as sodium thiosulphate pentahydrate, which dissolves in its own water of crystallisation at 48°C, and is therefore continuous with fusion, down to substances like barium sulphate, and in the extreme case, the metals, which are insoluble, for all practical purposes.

The concentration of solute which the solvent can hold is determined by the temperature. A plot of equilibrium concentration of solute in solvent against temperature is known as the "solubility" curve, and solutes can show increase, decrease, or remain almost constant in solubility with rising temperature. Such a curve shows the total solubility, which with an ionisable salt includes both ionised and non-ionised portions.

Now it has long been known that a saturated solution, free of crystals, can be cooled slightly without depositing crystals, and the solution is then oversaturated at the lower temperature, or in a state of supersolubility, or supersaturation. A saturated solution can also be made supersaturated by abstraction of solvent, or by addition of a second solute with a common ion.

The pioneer work on supersolubility was performed by Ostwald,[4] and further elaborated by Miers.[5] The viewpoint of Miers is shown in Fig.1. The system consists of three regions; unsaturated, metastable, and labile. The solubility curve separates the unsaturated and metastable regions, and the metastable limit, or supersolubility curve, separates the metastable and labile regions. A crystal placed in unsaturated solution will dissolve; a crystal placed in metastable solution will grow, but no new crystals will be formed; and in the labile region new crystals are readily formed spontaneously, or by the slightest shock or disturbance. The further the labile region is penetrated, the more unstable it becomes, although there is the possibility that increasing viscosity with supercooling will tend to freeze the nucleation rate, and a glass, or non-crystalline solid, will be produced.

The main objection to the theory of Miers is the abruptness of the change from one region to the other, as represented by the supersolubility curve. For example de Coppet[6] found that strongly supersaturated solutions nucleated rapidly, but less strongly supersaturated solutions also showed spontaneous nucleation, but after a greater length of time. He considered that the probability of nucleation increased with supersaturation, but without any definite limit for spontaneous nucleation.

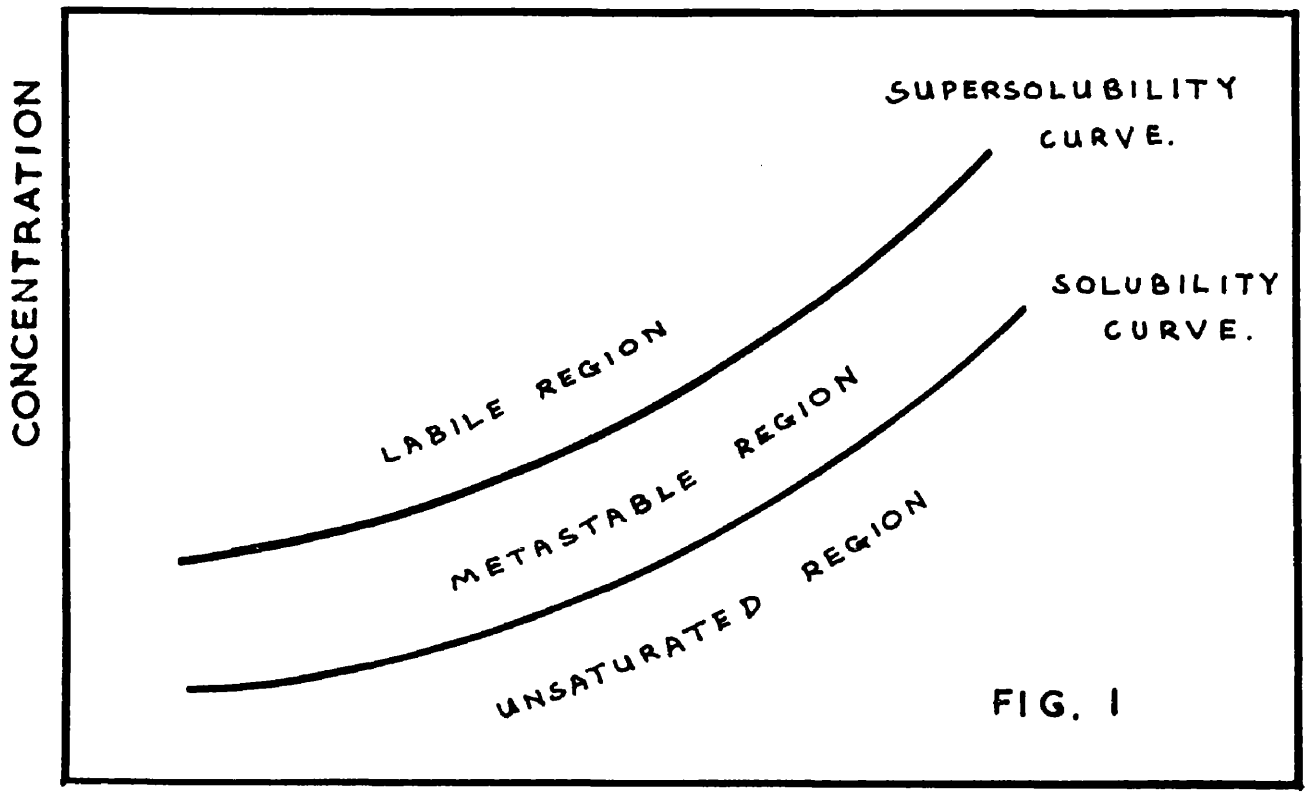

CONCENTRATION
SUPERSOLUBILITY CURVE.
SOLUBILITY CURVE.
LABILE REGION
METASTABLE REGION
UNSATURATED REGION
TEMPERATURE °C

FIG. 1

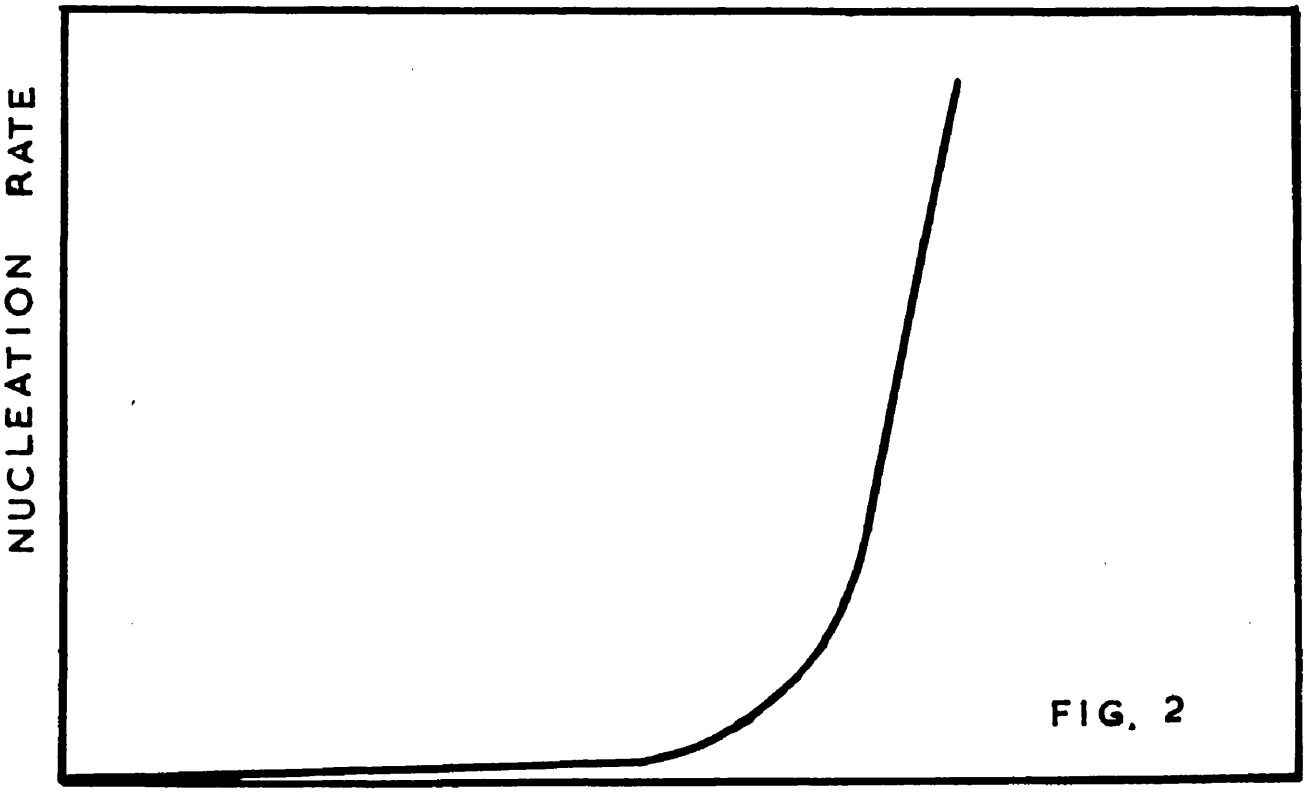

NUCLEATION RATE
SUPERSATURATION.

FIG. 2

Young[7] claimed that all the metastable region of Miers is capable of crystallisation if sufficiently strong mechanical shocks are applied, and that the well known inoculation of supersaturated solutions by small foreign particles, such as dust, is actually caused by mechanical impact between the particles.

Preckshot and Brown[8] found that solutions were more easily nucleated by crystographically similar substances than by spontaneous nucleation, and that nuclei always appeared, though at very small supersaturations the waiting time might be very long.

(b) Theories of supersolubility.

Experimental work by Hulett[9] and later by Van Hook[10] has proved that very tiny solute particles are more soluble than large particles.

The first theoretical expression for increase in solubility with decreasing particle size was given by Ostwald.[4]

Let r be the radius of a spherical particle and v_m its molecular volume.

The volume of a particle is $4/3\ \pi r^3$ and the number in a gram molecule is $3v_m/4\pi r^3$.

The surface of each particle is $4\pi r^2$, and the total surface of a gram molecule will be $O = 3v_m/r$

Let r_1 be the radius of a large particle and r_2 the radius of a small particle, and the corresponding solubilities be C_1 and C_2. Consider the transfer of a small quantity of particles of radius r_2 into the same mass of particles of radius r_1.

Then by equating osmotic work done and change in surface energy,

$$RT \ln \frac{C_2}{C_1} = 3 v_m \sigma \left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

where σ is the solid-liquid surface tension.

If the large radius r_1 is made infinite, C_1 becomes C_∞, or C_s, the normal solubility, and

$$RT \log \frac{Cr}{C_s} = 3 v_m \sigma \left(\frac{1}{r}\right) = \frac{3\sigma}{\rho_m r}$$

where ρ_m is the molar density.

Freundlich[11] modified this to read,

$$RT \log \frac{Cr}{C_s} = \frac{2\sigma}{\rho_m r}$$

but the essential argument remained the same.

The flaw in this argument is that infinitely small particles would have an infinitely large supersolubility. Knapp,[12] however, postulated an electrical charge on small particles, and, at some limiting particle size, the electrical repulsion between charges on very small particles overcomes the increased solubility

produced by particle size. Nuclei formed in supersaturated solutions will, of course, be very small, and will therefore tend to exhibit high solubility.

The increased solubility of nuclei has been approached from another angle by Van Hook.[13]

The Gibbs adsorption theorem states that

$$s = \frac{-C}{RT} \cdot \frac{d\sigma}{dC}$$

where s is the surface excess of solute over C, the concentration in the bulk of the solution. Then if the surface tension increases with concentration the surface layers contain less solute than the bulk, or, for a saturated bulk solution, surface layers are unsaturated. A minute nucleus will therefore be unstable, redissolving in the more dilute layers of solution which its own presence has created. Growth will only occur when the concentration of the surface layers becomes equivalent to the normal solubility concentration i.e. when the bulk solution is at some arbitrary level of supersaturation.

(c) Nucleation rates.

Although it has been seen that very small particles show supersolubility, in supersaturated solutions small particles can be formed and continue to grow.

If nucleation be looked on as the coming together of two or more molecules,

$$AB + AB + AB + AB++ \longrightarrow ABABABAB---$$

then it follows from normal energy concepts that in unsaturated solutions the solid complex on the right has a higher free energy level than the molecules in solution on the left. In a saturated solution there is only one level of energy, while in a supersaturated solution the solid, in some final bulk form, has less energy than the corresponding molecules in solution. Were the reaction in a homogeneous medium, equilibrium would presumably be established between right and left hand sides at some fixed concentration level.. The appearance of a solid phase must interfere with this simple homogeneity, introducing the complicating effect of a specific surface energy.

Now Dunning[14] has put forward the following analysis of liquid drop formation from vapour.

When a liquid drop of radius r_i is formed from i molecules of vapour, with a liquid-vapour interfacial tension σ, the vapour pressure p_i at the liquid surface is given by

$$\log \frac{p_i}{p_\infty} = \frac{1}{kT} \cdot \frac{2\sigma v}{r_i}$$

where p_∞ is the saturation pressure of the liquid at a plane surface, and v the volume of a molecule in the liquid. This equation may be written for any one liquid as

$$\log \frac{p_i}{p_\infty} = B \cdot \frac{1}{r_i}$$

where B is a constant. The ratio of vapour at the droplet surface to partial pressure in the saturated vapour varies as the reciprocal of particle size. For any supersaturated vapour at a pressure p_i there is a critical droplet size r_k for which the surface pressure is equal to p_i. Then larger drops than this will grow, while smaller drops will tend to evaporate.

If the chemical potential of a single molecule in the vapour phase is u_1, and in the liquid is u_2, the change in free energy when i molecules pass from the vapour to the liquid phase is given by $i(u_2-u_1)$.

When this is carried out by the formation of a liquid drop of area A, the increase in surface energy is ΔA, and the total energy change is

$$\Delta G = i(u_2-u_1) + \sigma A$$

If ΔG is to be negative, as must be the case if the change is to proceed spontaneously, then u_2 must be less than u_1.

For a spherical droplet,

$$A = 4 \pi r_i^2 \quad \text{and} \quad i = \frac{4}{3} \frac{\pi r_i^3}{v}$$

Then, $$\Delta G = \frac{4}{3} \frac{\pi r_i^3}{v} (u_2-u_1) + \sigma 4 \pi r_i^2$$

Values for ΔG will pass through a maximum positive value as r_i increases from zero to a critical value r_k, where

$$r_k = \frac{2\sigma v}{u_1 - u_2}$$

The maximum value of ΔG_k will be given, by substitution for r_k, as

$$\Delta G_k = \frac{16\pi\sigma^3 v^2}{3(u_1-u_2)} \quad \text{or} \quad \Delta G_k = \frac{16\pi\sigma^3 v^2}{3k^3T^3 \log^2 \frac{p_i}{p_\infty}}$$

Now treating the reaction

$$i\ AB \rightleftharpoons AB_i$$

as an equilibria, the law of mass action gives

$$n_i = k' n^i$$

where n_i is the number of i embryos per unit volume. The equilibrium constant k' may also be expressed in terms of the free energy of nucleus formation

$$-\Delta G = kT \log k'$$

and therefore

$$n_i = n^i \exp. \left(-\frac{\Delta G}{kT}\right)$$

If g is the probability that the critical nucleus will grow once formed, then

$$gn_i = gn^i \exp. \left(-\frac{\Delta G}{kT}\right)$$

or $$J = \beta \exp. \left(-\frac{16\pi\sigma^3 v^2}{3k^3T^3 \log^2 \frac{p_i}{p_\infty}}\right)$$

where J is the nucleation rate, and β is a constant.

As shown in Fig.2 when J is plotted against the measure of supersaturation $\frac{p_1}{p_\infty}$, the curve shows a rapid increase in nucleation rate when the supersaturation reaches a critical value.

Now this analysis has related supersaturation, nucleus size, and nucleation rate for a spherical drop forming from supersaturated vapour. The formation of a crystal of specific form from a vapour will depend upon the difference in energy between a molecule in the crystal face and a free molecule in the vapour. As before, there must be an expenditure of energy in the creation of the solid surface and $\Delta G = i(u_2-u_1) + \sigma_s A_s$, where σ_s is some measure of solid-vapour surface energy. It follows by analogy that a critical size for the crystal face, and a maximum value for ΔG will be

$$r_k = \frac{\sigma_s v}{u_1-u_2} \quad \text{and} \quad \Delta G_k = \frac{\sigma_s^3 v^2}{3(u_1-u_2)^2}$$

Very little is known about the surface energies of crystals except that they can vary from face to face. The shape factor also varies widely, and as a result the values for a spherical nucleus are often used as a basis for calculation. There is no doubt, however, about some value for a critical size and energy increment just as in liquid drops.

The addition of a second component, a solvent, to the one component system does not change the fundamental equation from

$$\Delta G = i(u_2-u_1) + \sigma_s A_s$$

in which the change in free energy of a molecule moving from solution to solid surface is balanced against the energy of free surface creation. In a nucleus of specific dimension r_i the number of molecules will vary as r_i^3, and the surface A_s as r_i^2. Then it follows that $\Delta G = C_1 r_i^3 (u_2-u_1) + C_2 \sigma_s r_i^2$ where C_1 and C_2 are shape factors.

When u_1 is greater than u_2 as in supersaturated solution, the value of ΔG plotted against some linear dimension r_i will pass through a maximum as before, and presumably the nucleation rate, J, should follow the same law, varying as the supersaturation rate, or rather as the square of the logarithm of this value. Several workers[15,16] have tried to establish the relationship experimentally, by plotting log J against the reciprocal of the square of the log. of the supersaturation, but results have not been very satisfactory. However, Dunning[17] suggested a modification in the nucleation rate term and achieved satisfactory linearity. He decided that the pre-exponential factor

β would depend on the supersaturation in such a way that

$$\log J + 3 \log.\log \frac{p_i}{p_\infty}$$

should be employed instead of log J in the linearity test.

The work of nucleation is available from momentary local fluctuations of concentration and energy. Naturally a chance association such as a foreign body, a dust particle, or a local disturbance caused by stirring or rubbing, will lower this critical value. Indeed there is experimental evidence[18,19] that all nucleation in supersaturated solution takes place by a heterogeneous, and not by a homogeneous mechanism. Crystals originate by heterogeneous crystallisation at an interface, e.g. on the surface of suspended, insoluble particles, or on the walls of the container.

Once a stable nucleus has formed it grows, with liberation of energy, and this liberated local energy may well catalyse further nucleus formation. The formation of "clouds" of tiny nuclei, so often seen in the crystallisation of inorganic salts, can readily be understood on this basis of energy chain reaction.

Experimental work on melts[20] has shown that the nucleation rate-supersaturation curve passes through a

maximum and falls away at high supersaturation, and Becker and Doring[21] allowedfor this by adding a viscosity term to the work expression,

$$J = \beta \exp. - \left(\frac{\Delta G_k}{kT} + \frac{E_\eta}{kT} \right)$$

where E_η is the activation energy for diffusion.

That this second factor can also be effective in nucleation from solutions[22] is shown in Fig.25 (page 74.) where the viscosities of saturated sodium thiosulphate solution are plotted against temperature. The dotted lines, showing increase in viscosity with supersaturated solution, rise steeply, suggesting that the formation of a solid glass is not far off. It may well be that the change in viscosity, varying widely from one substance to another, can explain the fact that some salt solutions cannot have supersaturation ratios increased above 1.01, while sucrose solutions, which are very viscous, do not form nuclei below a supersaturation ratio of about 1.3.

Furthermore, an activation energy of 4.4 kcals./gm. mole has been found for sucrose nucleation. This shows the importance of diffusion in nucleation, since the temperature coefficients of diffusion and viscosity of sucrose solution give activation energies of the same magnitude.

A reduction in the surface energy should increase the nucleation rate greatly. Some workers claimed[23,24] that the addition of surface active agents did increase the nucleation rate of sucrose, while others[15] found no effect. Van Hook[25] suggests that these surface active agents only decrease the static surface tension, and not the dynamic surface tension, which is the significant value regarding nucleation.

The relative shape of the solute molecule has also been considered[26] as important in nucleation, some molecules packing more easily into an ordered system than others.

(d) Nucleation in heterogeneous systems.

Industrial crystallisers always operate with seed crystals present, and therefore true spontaneous nucleation will never occur. It was found by McCabe and Ting[27] that the presence of crystal seeds lowered the critical value of supersaturation producing notable nucleation, probably by crystalloids from the crystal surface seeding the solution. The massive nucleation occurred at a definite, reproducible supersaturation when seed crystals were present, and at lower supersaturations than this value there was only a little random nucleation. The limit was affected by the rate of cooling, rate of stirring, and weight and

size of the crystal seeds used.

There is no doubt that nucleation rates increase rapidly even in crystal-solution slurries, when a certain level of supersaturation is reached. This level may be affected by such variables as those indicated by McCabe, or by factors such as active dust or chemical additives. These last may act in either direction.[es]

Summarising, theory suggests that there is both a critical size for stable nuclei, and a sharp increase in nucleus formation when certain supersaturation levels are reached. It appears that these conclusions are unaffected by the presence of preformed crystals. From the point of view of industrial crystallisation, the old concept of a metastable range of supersaturation is quite sound; a nucleation rate which is relatively slow makes for apparent metastability. If in the body of this thesis, a solution is referred to as "metastable" it will be understood that nucleation rates are too small to be considered.

Supersaturation can be measured as a ratio,

$$\frac{\text{Concentration in gms./litre in a supersaturated solution.}}{\text{Concentration in gms./litre in a saturated solution at the same temperature,}}$$

or as an actual excess of concentration - gms./litre.

The first form is more desirable from a theoretical standpoint, but when mass transfer rates are being considered the second form is proper. In the body of work following, the simple supersaturation, in gms./litre is normally used.

3. Crystal Growth.

The principal parameters affecting rates of reaction in concentrated solutions are temperature and concentration. The effect of temperature can usually be described by an Arrhenius equation, and concentration by $f(c) - f(c_c)$, where $f(c)$ is some function of the active concentration, and $f(c_c)$ is some function of the equilibrium value, ie. the normal solubility in the case of crystallisation. The rate of reaction will then be some function of the supersaturation, $f(C - C_s)$, and for most crystallisation processes the rate of growth can be described by

$$\frac{dx}{dt} = B\,(C - C_s)$$

where B is a constant, and dx is the amount of solute crystallised in time dt.

There are two main theories of crystal growth, one laying emphasis on the solution surrounding the crystal, and the other stressing the importance of the crystal surface itself. The first is concerned with the rate of solute transport in the solution, the other with the past history of the crystal, and the type of crystal surface which has been produced.

(a) Diffusion theories of crystal growth.

Noyes and Whitney[22] measured the rate at which crystals dissolved and proposed an equation of the form

$$\frac{dx}{dt} = K\,A\,(C_s - C_2).$$

Here A is the surface area of the crystal, C_s is the saturation concentration, and C_2 is the concentration in the bulk of the solution. K is a constant having the dimensions of a mass transfer coefficient, and dx and dt have the same meaning as before. No allowance is made for any time required to remove the molecules from the ordered array of the crystal.

Nernst[30] considered that the growth of crystals could also be considered as a diffusional mechanism, and modified the above equation to read

$$\frac{dx}{dt} = \frac{DA}{\delta} (C_2 - C_s)$$

where D is the coefficient of diffusion, δ is the film thickness through which diffusion is taking place, and the other symbols have the same meaning as before.

If there is diffusional control of crystallisation and solution then there should be a reciprocity of growth and solution at equal degrees of under and oversaturation. It has been found that dissolution is some six times as fast as growth. However, most of these reciprocity experiments were performed at circa 10°C, and it has been suggested[31,33-35] that at higher temperatures the growth process tends to become diffusion controlled.

Marc[32] added impurities to crystallising solutions and found that they inhibited growth greatly, while

having little effect on the rate of solution. This he took to be further evidence that the rate of growth is not diffusion controlled, but surface reaction controlled. There is no doubt[36] that specific impurities can greatly decrease the growth rate, and a surface reaction control may replace diffusion.

A further criticism of the diffusion theory is that with intense agitation the surface film should become very thin. It is commonly found that the growth rate increases with stirring speed only up to some limiting value,[5,37] and does not increase continuously. There is the possibility that film thickness does not vary inversely with stirring speed ie. the crystals may be carried round rapidly in their own relatively stagnant solution "atmosphere". In the production of large single crystals[38] the direction of rotation is reversed frequently to present the formation of veiled crystals caused by the mutual circulation of solution and crystal.

The principal objection to the Nernst theory in any unmodified form is that crystal growth is anisotropic, whereas if the growth rate were diffusion controlled completely, crystals should be spherical and have no plane faces.

(b) Berthoud's[59] modification of the diffusion theory.

Berthoud considered that there is not an infinitely rapid reaction at the crystal surface, but that time is needed to arrange the molecules during growth, and disarrange them during solution. This implies a reciprocity between growth and solution.

The concentration in the bulk of the solution and the saturation concentration are C_2 and C_s as before, but the concentration at the crystal interface is C_1, greater than C_s, but less than C_2. The diffusional process is followed in series by a first order interfacial reaction. If k_R is the interfacial reaction velocity coefficient then

$$\frac{dx}{dt} = k_R A (C_1 - C_s) = \frac{DA}{\delta} (C_2 - C_1)$$

when the stationary state is produced.

Hence

$$\frac{1}{A}\frac{dx}{dt} = \frac{D}{\delta + \frac{D}{kR}} (C_2 - C_s)$$

$$= K (C_2 - C_s)$$

The surface reaction coefficient k_R can vary from face to face, and therefore allows for the anisotropic nature of crystal growth. Berthoud's assumption that k_R will be the same for growth and dissolution need not necessarily be true.

If k_R is infinitely large then the reaction at the surface is infinitely rapid and the reaction is diffusion controlled, and vice versa. It is possible that the surface reactions of the faces of a crystal may vary greatly, with the result that growth at some faces may be diffusion controlled and at others surface reaction controlled. In this case the degree of supersaturation could change the shape of the crystal greatly, since the rate of growth of the surface controlled faces would remain almost constant, $[\propto (C_1 - C_s)]$, while the diffusion controlled faces would be free to vary with the supersaturation $[\propto (C_2 - C_s)]$.

This hypothesis would seem to answer Spandenberg's criticism[40] of Berthoud's theory, namely that a change in supersaturation produces a change in crystal habit, whereas the theory, as originally suggested, shows a uniform change in facial growth rate with supersaturation.

Berthoud's representation of crystal growth as a diffusional process followed by a crystal surface arrangement has been justified by several workers.[35,37,41] Humphreys-Owen[15] has also found that some faces of sodium chlorate follow the Nernst mode of growth, and that others apparently grow faster than the solute is presented to them by diffusion, i.e. they may grow dendritically to enter fresh spheres of supersaturation.

Leblanc and Schmandt[31] found that sodium chlorate was one of the few solutes which showed a reciprocity between growth and solution.

Jenkins[42] claimed that by rapid stirring he had so reduced the film thickness that he was actually measuring the rate of surface reaction. Nevertheless he was able to correlate his crystallisation rates against $\frac{1}{\eta^{0.59}}$, where η is the solution viscosity. The viscosity is a function of the solution, and should therefore have no effect on the rate at the crystal surface, and he could not therefore have been measuring the crystal surface reaction.

Some solutes have been found[32,43] to have a rate of crystallisation which is best represented by a bimolecular reaction. A bimolecular reaction indicates that the crystallisation rate must be surface reaction controlled. Jenkins[42] found only one case of bimolecular reaction, the crystallisation of naphthalene from methanol in the presence of collodion. The collodion produced a drastic habit change, and is another example of specific impurity greatly decreasing growth rate, thereby causing surface reaction control of crystallisation.

Summarising, the diffusion theory of Berthoud would seem to describe the problem of crystal growth adequately.

Growth takes place by diffusion of the solute to the crystal surface followed by crystal surface reaction. Either of these processes may control the rate of growth, according to the physical characteristics of the system.

(c) The surface reaction.

The concept of a crystal surface reaction combined with diffusion has already been established. Solutes are known which would seem to be completely surface reaction controlled in their crystal growth. Sucrose is one of the most important substances which is produced in a crystalline form, and it has been found by Van Hook[44] that a 25 fold increase in the solution viscosity makes no difference to the crystallisation velocity. The activation energy for crystallisation is of the order of 15 Kcals./mole, while that for diffusion is 6 Kcals./mole. Van Hook concludes[45] that the crystallisation process is surface reaction controlled at the normal temperature range for sucrose crystallisation.

(d) Adsorption layer theories.

Marc[46] considered that the diffusion layer was torn off by very rapid stirring, leaving a layer of almost molecular dimensions, which had the nature of an adsorbed layer. Interaction between the molecules in this layer and the crystal lattice was relatively slow.

Volmer[47] grew mercury crystals from the vapour, and observed that the crystals grew layer by layer, though the layers were certainly not on a molecular scale. According to Volmer when a particle arrived at the crystal surface it only lost part of the latent heat, and was free to move over the crystal surface like a "two dimensional gas". From collisions between the particles of this adsorbed layer a nucleus could be formed; the velocity of growth of the nucleus once formed, was proportional to the square of the density of the particles in it.

The concept of growth by "two dimensional" nucleation is similar to that for three dimensional homogeneous nucleation, and has been developed by several workers.[21,48-53] Atoms condensing on a surface will prefer states with a maximum number of nearest neighbours,[54] e.g. position a in Fig.3A. Repetition of similar steps will cover the surface with a close packed layer, Fig.3B, and growth will temporarily stop until a new two dimensional nucleus is formed on the surface, Fig.3C. Kossel[54] and Stranski[49] have deduced that the most favourable positions for surface nucleation in an ionic crystal will be the corners and edges rather than the face centres.

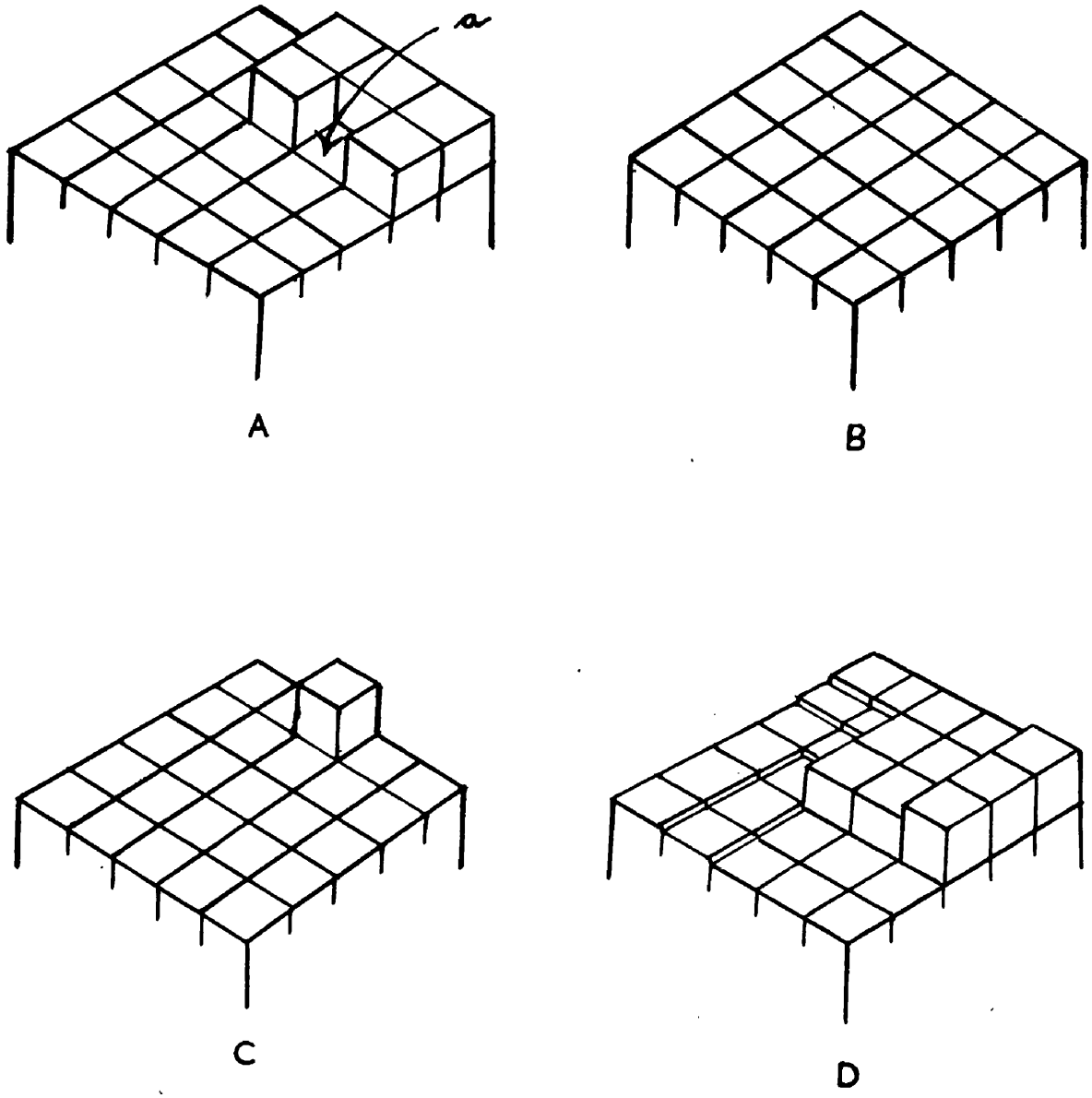


FIG. 3.

The free energy of the nucleus will be

$$G = 2\pi r a \sigma + \pi r^2 a (u_2 - u_1)$$

where r is the radius of the nucleus, a is the interlayer spacing, σ is the surface free energy, and (u_2-u_1) is the change in chemical potential.

Then the critical nucleus radius and free energy are given by

$$r_k = -\frac{\sigma}{u_2-u_1} \qquad \text{and} \qquad \Delta G_k = -\frac{\pi \sigma^2 a}{u_2-u_1}$$

and the rate of nucleation by

$$J = \beta \exp. \left(\frac{-\Delta G_k}{kT}\right)$$

Before nucleation can occur the supersaturation should be of the order of 40-50%, i.e. a metastable limit for surface nucleation, but it is known[55] that crystal growth takes place at supersaturations of less than 1%.

(e) Dislocations.

If the Miller indices of a crystal face are high then the face will grow rapidly, whereas low Miller indices give slow growth. The modern theory of crystal growth is that nucleation on low index surfaces is unnecessary, since high index surfaces are always present because of screw dislocations. The concept of screw dislocations was introduced by Burgers[56] to account for the very low strength of crystals compared with the theoretical value, and its importance in crystal growth

has been demonstrated by Frank[57] and others.[58,59]

A screw dislocation is formed when the dislocation is parallel to the dislocation line, and a block model is shown of a typical screw dislocation in Fig. 3D. Addition of atoms to the edge of the screw dislocation will develop a self-perpetuating spiral growth, since the dislocation perimeter will have a higher angular velocity than the centre. The screw dislocation will be able to grow at a low supersaturation, as indeed crystals are able to do.

Screw dislocations have been observed[60-63] on such diverse substances as sodium chloride and long chain paraffins. Many of the growth spirals have a large step height, and may be caused by multiple dislocations during nucleation, or by successive layers piling on top of each other. Dawson and Vand[64] have, however, observed molecular step heights by means of an electron microscope.

(f) Effect of impurities on crystal growth.

Specific impurities are known[28,66,65] to slow down, and may indeed stop crystal growth. The impurities are specific to each solute, and even specific to certain crystal faces, thus changing the crystal habit. The impurities may adsorb[66] on the step of the screw dislocation and slow down growth, and in so doing can

produce[65] better quality crystals.

If the crystal grows by surface nucleation the newly formed nucleus may be rendered inert by impurity adsorption.

(g) Layer growth.

Relatively thick layers have been seen spreading over crystal surfaces.[67] These layers may be complicated screw dislocations, yet investigation has shown that this layer growth takes place under conditions which are not concordant with the presence of screw dislocations. Bunn[68] and Berg[68] evolved a technique of concentration measurement by means of interference fringes when a crystal was growing between glass plates. Bunn found that the concentration was not uniform along a face, but was lowest at the centre, and that the concentration gradient normal to the face was highest at the centre.

Furthermore, similar crystallographic faces often had different growth rates, and there was a tendency for the slower growing faces to be in contact with solution of highest concentration, and in the extreme case faces which stopped growing had the highest local concentration.

It was concluded from these observations that there is a surface migration of solute to the crystal corners, having the nature of an adsorbed layer, and

that the initiation of layers at the centre of the crystal, and the subsequent variation of growth rates is due to the relative movement of solute molecules in solution and over the surface. According to Bunn, growth takes place on high index surfaces which are continually formed during layer growth, and the cessation of growth observed is caused by healing of these high index surfaces to form low index surfaces.

Frank[43] replied to this criticism of the dislocation theory by claiming that convection would occur in Bunn's experiment, and would alter the presentation of solute from a purely diffusive process. He considers that sudden changes in growth rate are explained by rearrangement of dislocations, or stoppage of growth by impurity poisoning of the dislocation site. The photographic records taken by Emmet[41] of crystals growing show a very ordered form of layer growth as in screw dislocations, and not an indiscriminate layer expansion as it should be if Bunn's hypothesis were correct.

Williams[70] investigated layer growth on lead nitrate, and found that growth could occur either by nucleation at the corners and edges as in the Kossel--Stranski model, or by a screw dislocation mechanism. Initially the crystal grew by nucleation and layer

completion, but after the supersaturation decreased growth took place by the formation of a screw dislocation with a large step height. In addition the mode of growth could be changed from surface nucleation to screw dislocation by scratching the crystal surface with a sharp steel point.

4. The Effect of Nucleation Rate and Suspension Conditions on Product Crystal Size.

If the inherent seed rate of a crystalliser under working conditions is N nuclei/hour, and the production rate is P lbs./hour, the average weight of a product crystal will be $\frac{P}{N}$ lbs. Large, well formed crystals are the operational target, and it is often found that the inherent nucleation rate is too high to give the desired size of product crystal. Crystallisers have been built (e.g. the Howard crystalliser, and to some extent the Oslo crystalliser) which use hydraulic elutriation to govern product crystal size. These devices will only perform as planned if the nucleation rate is low enough for the desired product, otherwise the crystalliser will become overloaded with an excess of small crystals. It is rare to find troubles associated with too slow a nucleation rate.

However, a proportion of the fine crystals may be removed in a segregation chamber, and a mathematical analysis has been presented by Saeman[71] of product size control by this means in single vessel crystallisers.

If N_f and N_p are the number of fines and product crystals removed per hour, and l_f and l_p their respective sizes, then

$$\frac{F}{P} = \frac{N_f \, l_f^{\,3}}{N_p \, l_p^{\,3}}$$

where F and P are the weights of fines and product

crystals produced per hour.

In an Oslo crystalliser, operating with a classified suspension of crystals in the bed, fines may be segregated from the suspension when they are of the order of one tenth product size. If there is a hundred fold excess of fines then

$$\frac{F}{P} = \frac{100}{1} \times \frac{1}{1000} = 0.1$$

Therefore by removal and resolution of 10% of the crystallised material the product crystal size may be increased by a factor of $100^{0.33} = 4.6$

It can be proved that in a classified suspension the cumulative crystal weight varies as the fourth power of the crystal size e.g. crystals up to one-half product size constitute only one sixteenth of the total weight in suspension. Also the age of product crystals is four times the draw-down time T, where $T = \frac{W}{P}$ and W is the weight of crystal in suspension.

The removal of small crystals in the product from a mixed suspension produces a greater proportion of small crystals in the suspension than that allowed for by the fourth power relation. However, the crystal product will be approximately the same as in a classified suspension. The product will show a dominant crystal size equivalent to an age of 3T as against 4T for classified product removal. There will be no small

crystals withdrawn in classified crystal product removal, and in mixed product removal the small crystals will be large in number, but almost negligible on a weight basis.

In addition the seed requirements for mixed product removal are about eleven times the number required for classified production. A full derivation of the above relationships is given in Appendix C.

Classified production will give large crystals with no fines present. Mixed production, with eleven times as many seed crystals, will give product crystals of almost the same size, but with a small fraction of fine crystals. It follows that in a case where classified production gives too small crystals because of a high seed rate, the dominant product size will be increased by changing to mixed product removal.

Robinson and Roberts[72] have developed Saeman's work further, and given crystal size distributions for a series of continuous flow stirred crystallisers.

An Oslo crystalliser will normally work at some condition intermediate between a fully classified bed, and a fully mixed bed.

B. Experimental Technique.

1. Experimental Programme.

The purpose of the work was to provide design data for the production of sodium chloride, sodium thiosulphate pentahydrate, and barium hydroxide octahydrate in an Oslo crystalliser.

The main points to be investigated for each solute were the rate of crystal growth, and the effect of temperature and solution velocity thereon; the metastable limit of supersaturation; maximum crystal production rates; and the shape and size of crystal which would be obtained from a continuous crystalliser.

The two general methods for measuring rates of growth have been either following the growth of a single crystal at a known supersaturation, or measuring the change in concentration of the supersaturated solution when a mass of crystal seeds is present. The first method gives absolute rates of crystal growth, but if the crystallisation process is surface reaction controlled it places too much emphasis on the crystal which is used in the experiment. The second method is convenient for studying the order and mechanism of growth, but small seeds and fresh nucleation make estimation of absolute rates of growth rather doubtful.

Griffiths[73] after long experience in the problems of industrial crystallisation, was of the opinion that the rate of crystal growth is a very fickle constant to measure and said "it might be thought that determination of the rate of crystal growth in a metastable solution would be easy. As soon as attempts are made, it is found to be extremely difficult to get consistent results, and a little experience soon convinces us that consistent results cannot be obtained without extremely thorough agitation."

Crystals were grown in fluidised beds in three different types of apparatus. In the first, saturated solution was cooled to give the desired degree of supersaturation and passed once through a fluidised bed of crystals. The change in supersaturation passing through the bed was only of the order of 2-3%. The increase in weight was measured over a given period of time, and since large, uniform crystals were used in the experiment, the surface area could be estimated and the mass transfer coefficient calculated.

Any small crystals formed by spontaneous nucleation were carried away by the upwards flow of solution. The experimental results should give a good basis for plant design since the weight increase is measured directly; the surface area of the crystals is known,

and the average growth rate of a large number of crystals is found.

The other two units were continuous models, and were used to obtain production figures which could be scaled up for a large plant. As with the small unit, they were fluidised bed crystallisers, but the amounts of crystal and solution involved were much larger, with steady feed of fresh solution and withdrawal of crystal slurry.

The supersaturation can increase cyclically in a continuous plant, and estimation of the mass transfer coefficient is therefore difficult, since the supersaturation may represent only 1% of the total solute present, while fine crystals are carried round the plant with the solution. Provided no fine crystals were present in the sample an accuracy of $\pm$ 10% in the supersaturation value for sodium chloride would require an accuracy of circa 1 in 3,000 in the estimation of salt in solution. The operational conditions in the continuous crystalliser could be calculated, however, by applying the growth rate results obtained in the non-continuous model.

Nuclei formed spontaneously in the continuous crystallisers and grew to product size, and therefore the equilibrium shape, size, and quality of product crystals could be determined. The effect of production

rate on product size was investigated, and also the maximum production rate possible before excessive nucleation and salt incrustation occurred.

2. Experimental Apparatus and Methods.

(a) Cooling crystalliser.

The apparatus is shown in Figs. 4 and 5. A vacuum pump system sucked saturated solution from a constant temperature bath A, through a cooler C and a crystallisation tube D into a receiver E. The tank A was thermostatically controlled to $\pm$ 0.05°C, and was covered to reduce evaporation. A stirrer suspendod crystals in the sclution, and ensured temperature and concentration uniformity. The solution was drawn through a fine nylon screen into a 2" diameter disengaging tube B. By this means a clear, saturated solution flowed to the cooling and crystallising section.

The cooler C was a water jacketed glass or copper pipe. The crystallisation tube D was 1 inch in diameter, and a bed of preformed crystals was supported initially on a 20 mesh Monel screen. Solution entered tangentially at the base of the tube, passed upwards through the now fluidised mass, and flowed from the top of the tube into the receiver E.

The temperature of the solution in the bath, the

BATCH COOLING CRYSTALLISER

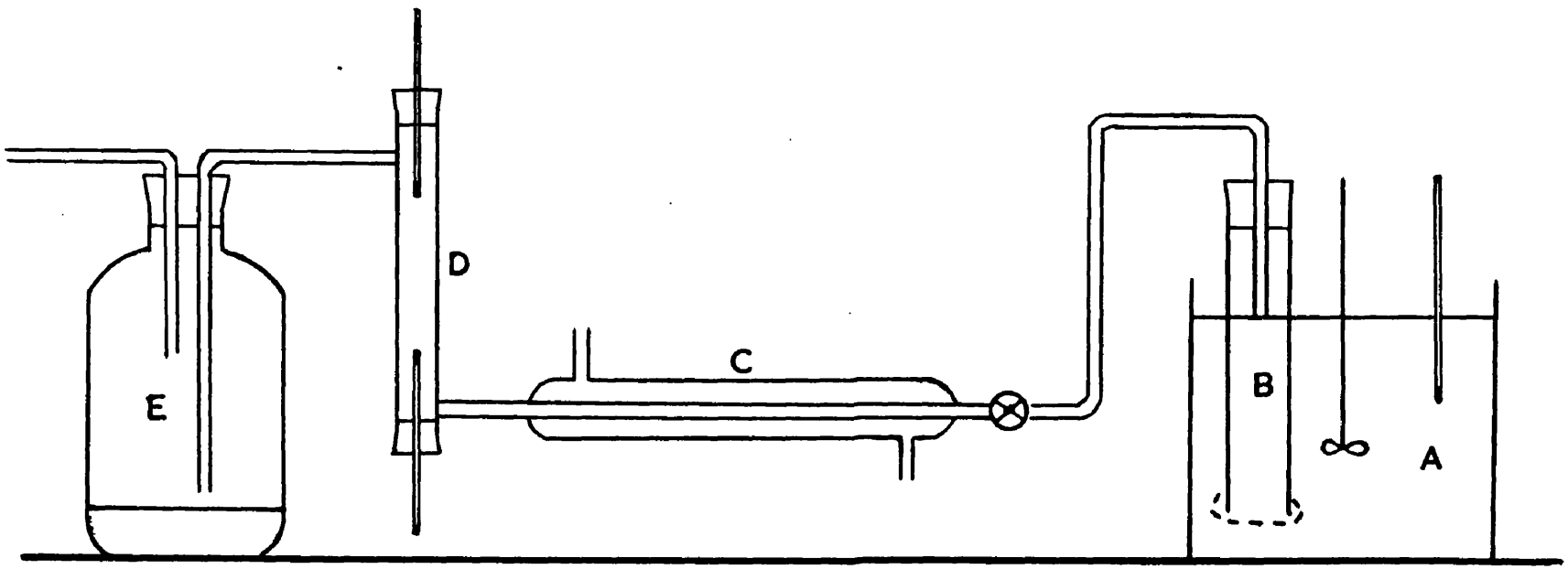
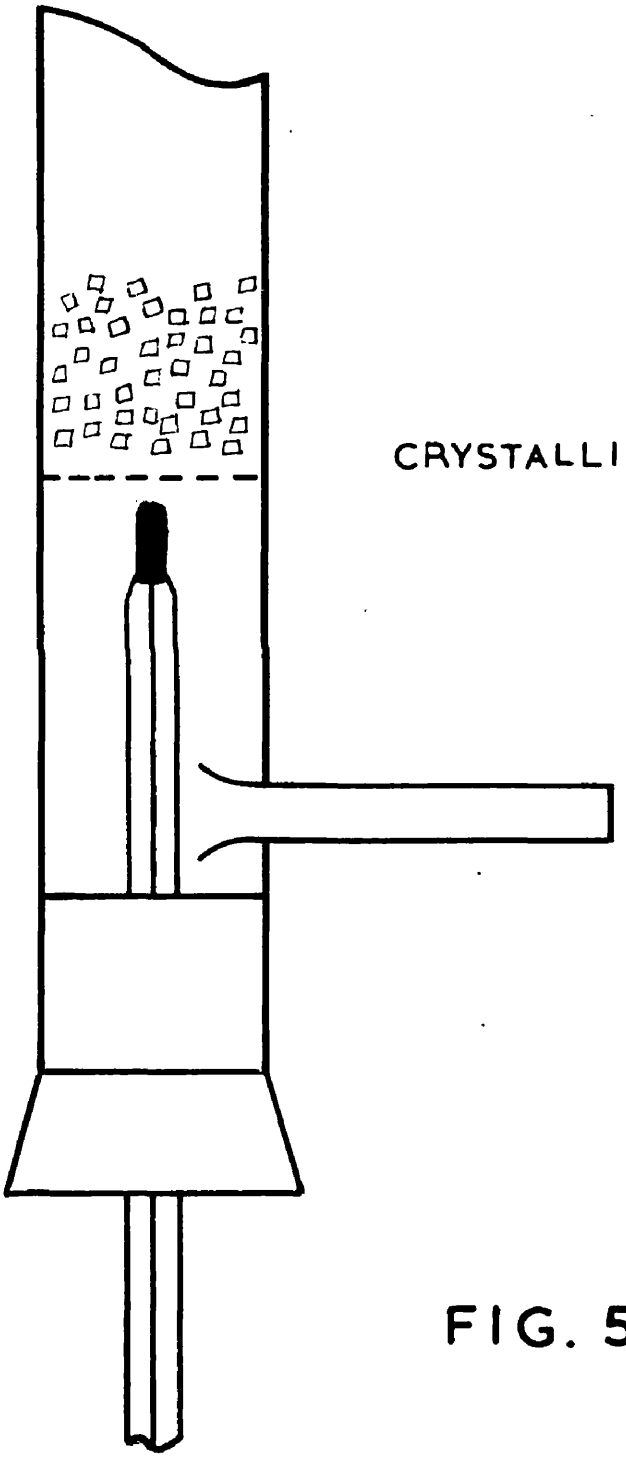


FIG. 4.



CRYSTALLISATION TUBE.

FIG. 5.

solution entering the bed, and the solution leaving the tube were measured on thermometers graduated to 0.01°C, and standardised against each other.

The solution flow was controlled to give the same height of fluidised bed in each run.

Crystals used in the experiments were prepared in the small Oslo evaporative crystalliser described in the next section, and therefore possessed the same shape as product crystals from an Oslo crystalliser.

Both crystals and solution were prepared from industrial grades of the respective solutes, and solutions were made up with tap water - Glasgow Town Supply. This is a particularly pure form of industrial water with a total solid content as low as 100 parts per million.

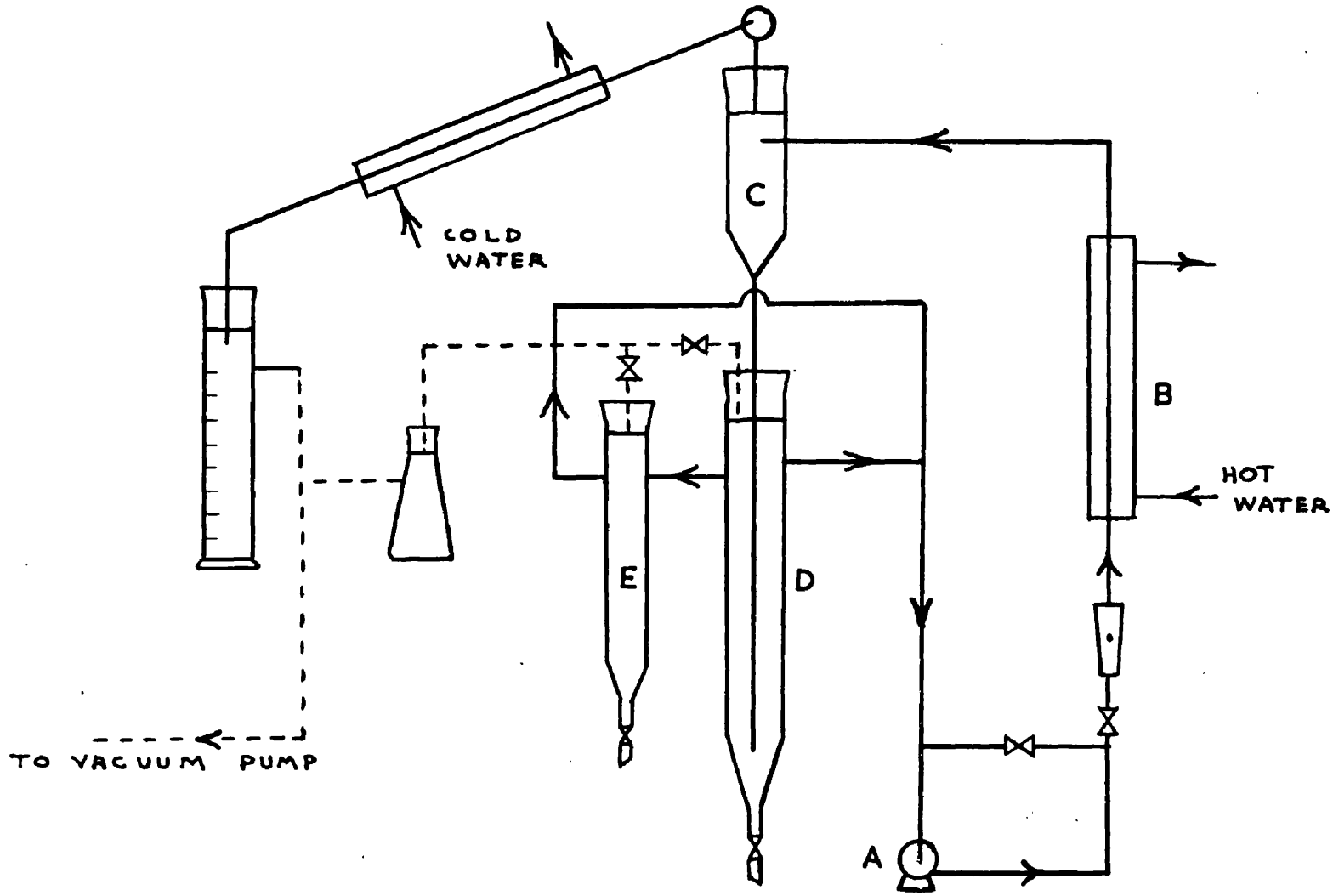
The crystals and solution in the bath were heated to a temperature which would give the required degree of supercooling on cooling to the crystallisation temperature, and held at this temperature for one and a half hours to ensure perfect saturation. 4 gms of crystals, normally 12-18 mesh, were weighed and placed in the crystallisation tube, and the solution and cooling water flows set at the required rates. The test lasted 15 minutes, and the crystals were straightway removed, filtered, washed with methanol, dried, and weighed.

(b) Laboratory Oslo crystalliser.

This plant is shown in Fig.6 . A small centrifugal pump A, later changed to a 0.33 H.P. Mono pump circulated saturated solution through a heater B to a flashhead C, where part of the water was removed under vacuum. The supersaturated solution flowed down through the central downtake, and up again through the fluidised bed of crystals D. Part of the flow could be directed through a settling chamber E to remove fine crystals circulating in the stream. The solution flow was measured by means of a Ewing ball and tube flowmeter. Cold saturated feed solution was sucked into the plant at the base of vessel E.

The change from a centrifugal to a Mono pump was made because of the difficulty in keeping the gland of the centrifugal tight under vacuum. It was only possible to operate by putting the whole pump in an evacuated chamber - a very clumsy contrivance. When a Mono pump was installed the slower speed made air leaks easier to check, while the pump was self priming. It was not possible to operate with a fluid head that made normal atmospheric operation at the pump site possible (a 30 ft. head would be required).

The crystallisation vessel and fines separator were all in glass, the first of 2" diameter, 30" long, and the second 1.5" diameter and 10" long. The heater



LABORATORY CONTINUOUS CRYSTALLISER.

FIG. 6.

was a 12" length of $\frac{1}{2}$ " bore glass tube, with a jacket through which hot water was circulated from a thermostatically controlled reservoir. Evaporation rates up to 400 gms. of water per hour could be obtained with the crystalliser working at 38°C.

In the operation of the unit upwards rates of flow were controlled by the need for smooth fluidisation of a crystal bed, and were normally set at circa 3 cms/sec.

Under continuous production conditions the fine crystal separator E was discarded, and all nuclei formed were retained in the plant.

(c) Semi-technical plant.

The plant (Fig.7) was a larger version of the laboratory Oslo crystalliser, except that no fines separator was incorporated. The crystal suspension was held in a 1 ft. diameter, 4 ft. long glass vessel A, constructed from Q.V.F. sections. Air leakages entrained by the liquid flow, rose to the top of the vessel, where a tapping to the vacuum line removed gas as required. This was essential to the smooth working of the plant.

The pump B was a stainless steel Alfa-Laval centrifugal unit powered by a 0.8 H.P. motor running at 1410 r.p.m., with an output of 40 gallons per minute at a 5 ft. head. The solution flow was measured at

SEMI-TECHNICAL PLANT.

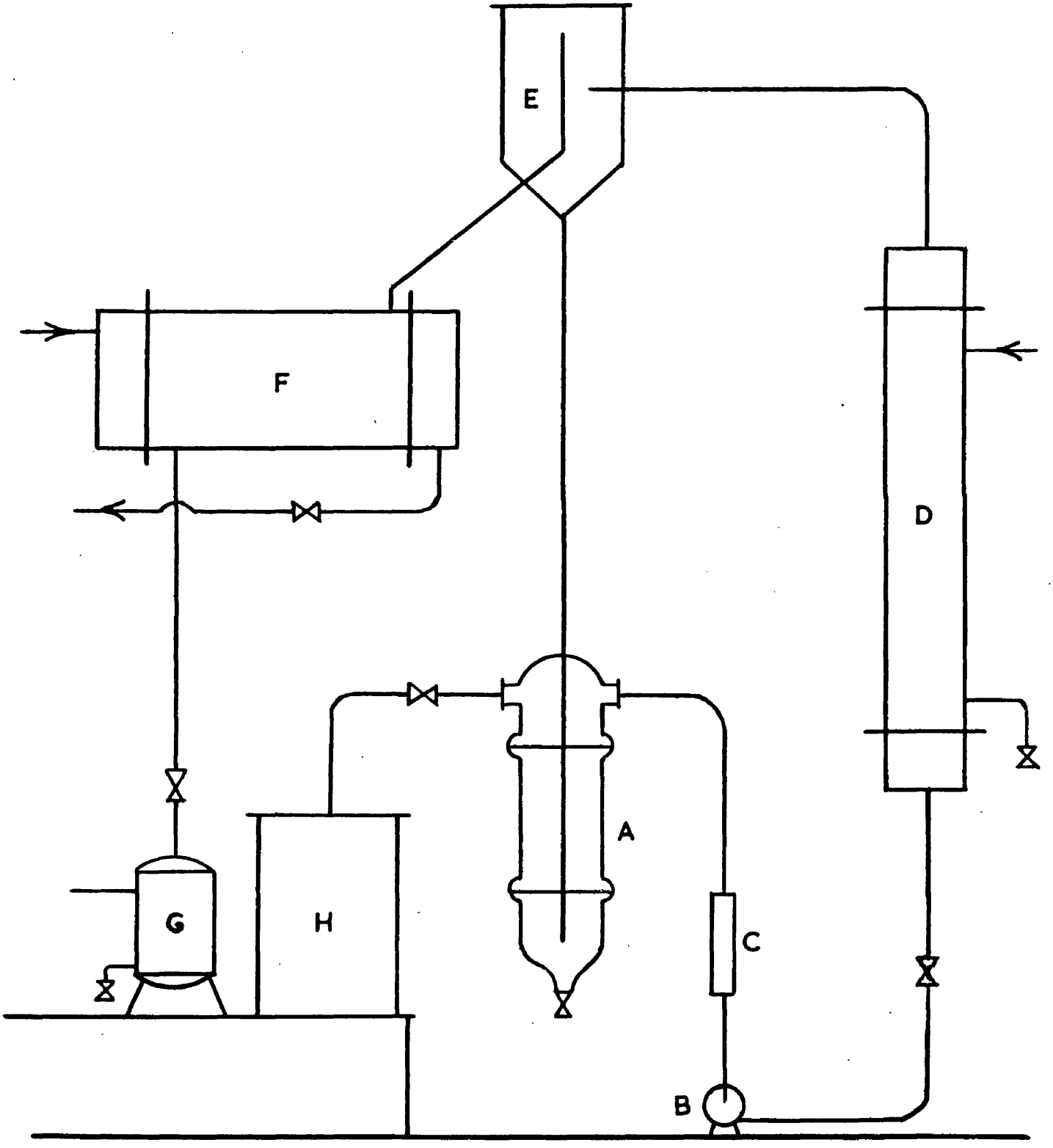


FIG. 7.

first by the extension of a previously calibrated spring float C, (Appendix a), and later by means of a Rotameter. Under operational conditions the flow was normally 33 g.p.m., equivalent to an upwards velocity through the crystalliser of 3.4 cms./sec. This pump, with a mechanical seal, gave no trouble in operation, though previous attempts with a closed impellor, packed gland type pump gave endless difficulty through crystal build up and leakage.

The heater D was a steam heated tube and shell heat exchanger with 4 stainless steel tubes 12 ft. long. The flashhead E was of rubber lined mild steel, 18 ins. diameter and 2 ft. long, and the solution entered tangentially. Solution, now supersaturated, flowed down to the crystalliser; the separated vapour was condensed in a steel tube condenser F, and collected in condensate receiver G.

Saturated feed solution was sucked into the glass vessel under vacuum from a rubber lined mixing tank H. Solution flow lines were either glass or rubber lined mild steel.

The plant operated under vacuum, and the operating pressure was adjusted by hand, after an attempt at automatic control had failed because of corrosion in the control valve, and the vacuum was provided by

a Broom and Wade rotary vacuum pump.

Crystals were removed periodically from the base of the crystalliser through a diaphragm valve into a detachable glass receiver. The product crystals were centrifuged to about 3% moisture, and then dried off in an electrically heated tray drier.

C. Experimental Results.

1. The Crystallisation of Sodium Chloride.

Sodium chloride is normally crystallised in vacuum evaporators to give a very fine crystal, about 30-60 mesh. This is the " Vacuum Salt" of commerce, and nucleation and crystal growth are relatively uncontrolled. On the other hand, slow evaporation in large open pans, with either direct firing or steam coil heating, produces a large irregular crystal, the time honoured " Fishery Salt" . The latter process is most uneconomic from a fuel efficiency and labour point of view, but there is a definite need for this size of crystal for food preservation and leather manufacture.

Attempt to grow large crystals in normal evaporators have been uniformly unsuccessful, because of the high inherent rate of nucleation of the solute, and large sodium chloride crystals from Oslo crystallisers provide the only opposition to " Fishery Salt" .
A defect of the Oslo salt is that the commercial product tends to be spherical, and therefore part of the salt rolls off the hides, etc. on which it has been thrown.

Crystallisation tests were carried out in all three apparatus.

The crystals used in the growth rate experiments

were grown in the laboratory Oslo crystalliser, and were cubical, with the corners and edges somewhat rounded. However, for calculation of surface area it was assumed that theywere perfect cubes, and also that the side of the cube had a length midway between the screen apertures of the mesh size.

It was further assumed that the shape of the crystal remained invariant with size. In these circumstances the weight of a single crystal of specific dimensions equivalent to a linear factor l, would be

$$W_1 = c_1 \rho l_1^3 \text{ , and the area } A_1 = c_2 l_1^2$$

$$\text{Then } l_1^3 = \frac{W_1}{c_1 \rho} = \left(\frac{A_1}{c_2} \right)^{\frac{3}{2}}$$

$$\text{or } W_1 = c_3 A_1^{\frac{3}{2}}$$

If the crystal grows from W_1 to W_2

$$W_2 = c_3 A_2^{\frac{3}{2}}$$

$$\text{or } \frac{W_1}{W_2} = \left(\frac{A_1}{A_2}\right)^{\frac{3}{2}}$$

$$\text{i.e. } A_2 = A_1 \left(\frac{W_2}{W_1}\right)^{\frac{2}{3}}$$

What is true for one crystal is true for any fixed number of crystals, and the surface area of the bed of crystals at the end of the run could be calculated from the initial area and the increase in weight.
In the calculations of rates of growth and mass transfer coefficients the average of the area at the beginning and end of the run was taken as the area on which growth

took place.

Solubility figures were taken from the International Critical Tables (1st. Edn., Vol.4, p.235).

1a. Experiments in a small cooling crystalliser. Rate of crystal growth.

The effect of supercooling on the rate of growth of sodium chloride crystals is shown in Fig.8. The crystals were initially 12-18 mesh (1.1 m.m.), and the solution velocity was 3 cms./sec. through the crystallisation tube when free of crystals. The rate of growth is expressed as gms. of solute crystallised per hour per gram of crystal in the bed at the start of the run, and the supercooling is given in degrees Centigrade.

Crystallisation was carried out at 26, 38, 45, 62 and 73°C.

These results have been recalculated in Fig.9 to give the supersaturation in gms. of supersaturated solute per litre of solution, and the growth rate as gms. of solute deposited per hour per square centimetre of crystal surface. As already stated, the active supersaturation is taken as the inlet supersaturation to the bed.

The variation of growth rate with temperature has been shown in Fig.10, at inlet supersaturations of

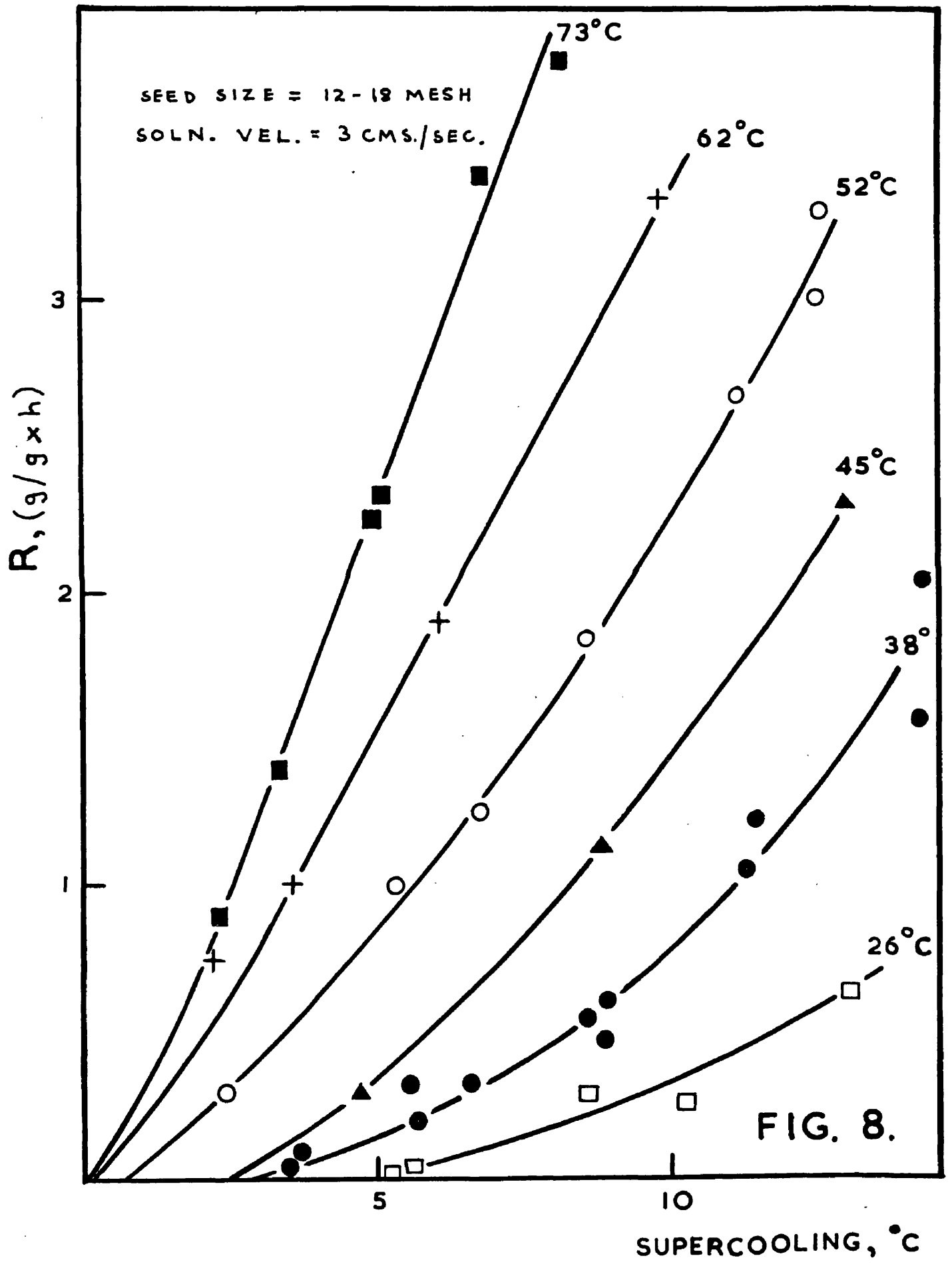

SEED SIZE = 12 - 18 MESH
SOLN. VEL. = 3 CMS./SEC.
73°C
62°C
52°C
45°C
38°
26°C
R, (g/g x h)
1
2
3
5
10
SUPERCOOLING, °C

FIG. 8.

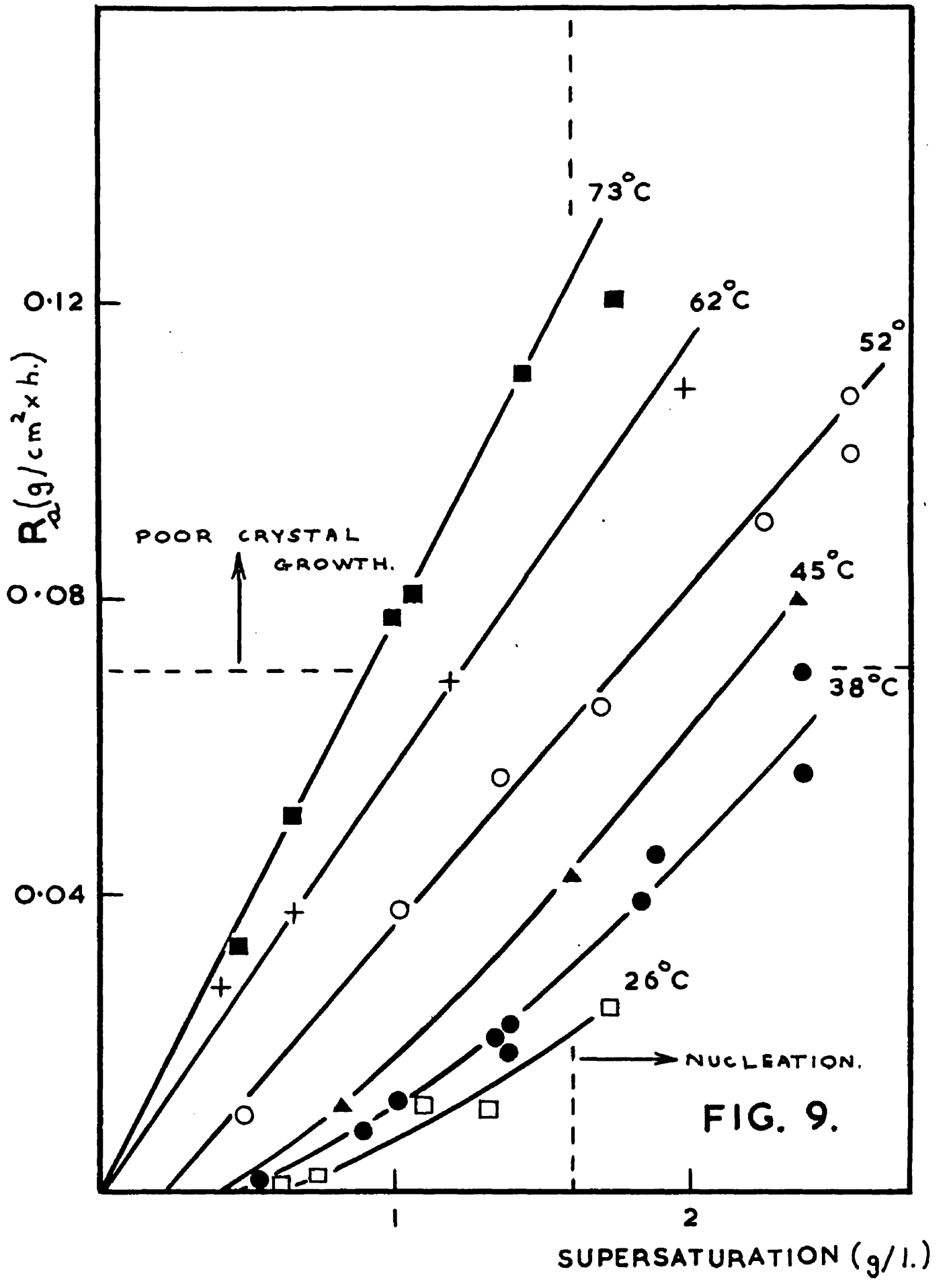

73°C
62°C
52°
45°C
38°C
26°C
0·12
0·08
0·04
R_d (g/cm² x h.)
POOR CRYSTAL GROWTH.
NUCLEATION.
1
2
SUPERSATURATION (g/l.)

FIG. 9.

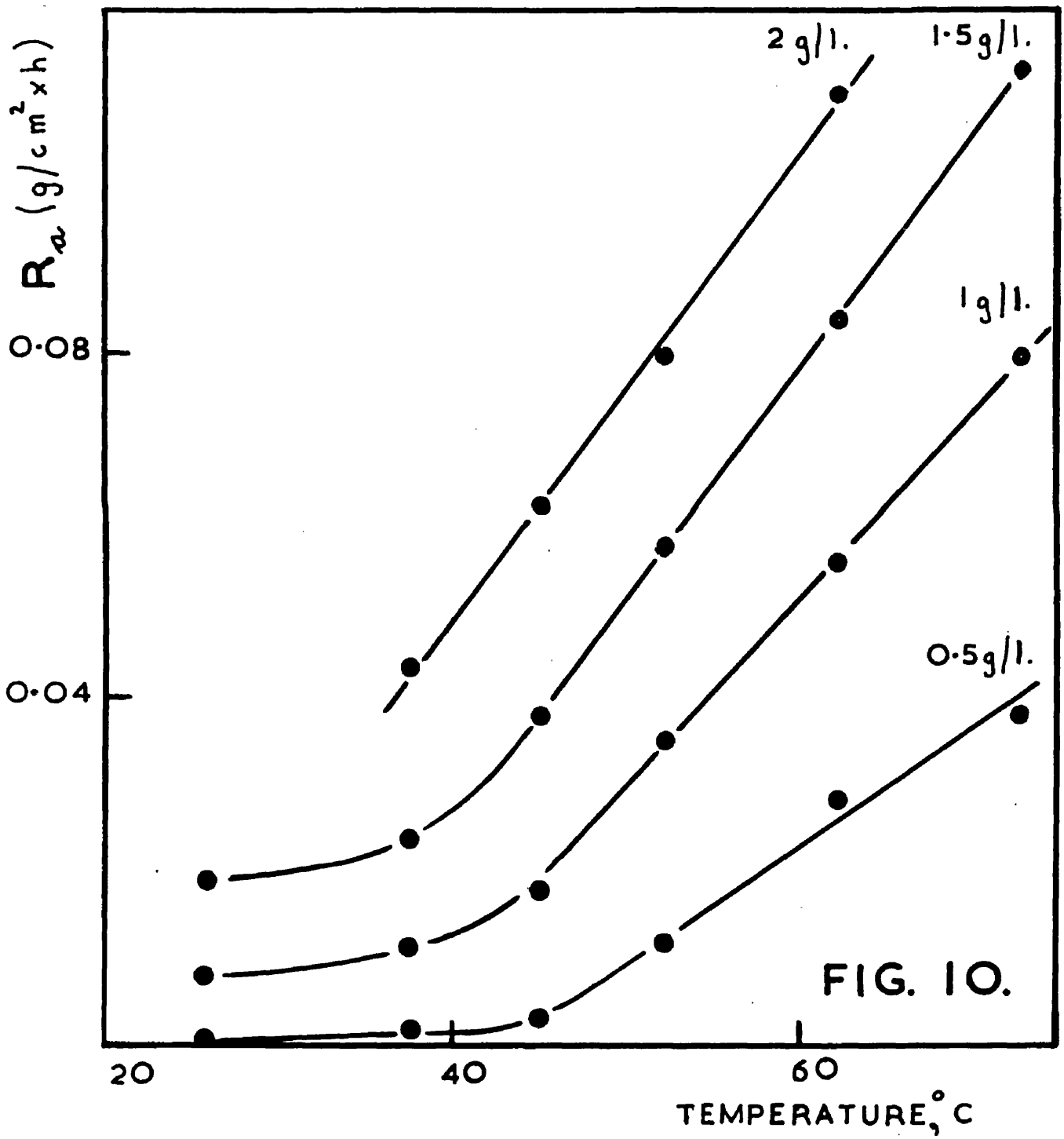


FIG. 10.

0.5, 1, 1.5, and 2 gms./litre.

Referring to Fig.9 it can be seen that the family of curves shows a gradual change, from the curve at 26°C with a zero growth rate at a supersaturation of 0.5 gms./litre, to the straight line at 73°C passing through the origin. For crystallisation at temperatures of 52, 62, and 73°C the dependence of growth rate on supersaturation is of the first order, and at the lower temperature of some higher order.

The overall mass transfer coefficients, i.e. including both diffusional and surface reaction resistances, have been calculated, and the dimensions of the coefficient, K, are gms./cm.^{2} x hr. x gm./c.c., or cms./hr. Note that this should be distinguished from a linear growth rate even though the units be the same.

In Fig.11 the logarithms of the mass transfer coefficients at 52, 62 and 73°C have been plotted against the reciprocals of the respective absolute temperatures. The slope of the line gives an activation energy for crystallisation of 5.4 kilocalories per gm. mole. Moelwyn-Hughes[74] states that activation energies of less than 6 kilocalories are typical of physical processes. Also an Arrhenius plot (Fig.11) of the diffusivity data for sodium chloride solutions containing 0.05 gm . equivalents per litre (I.C.T.)

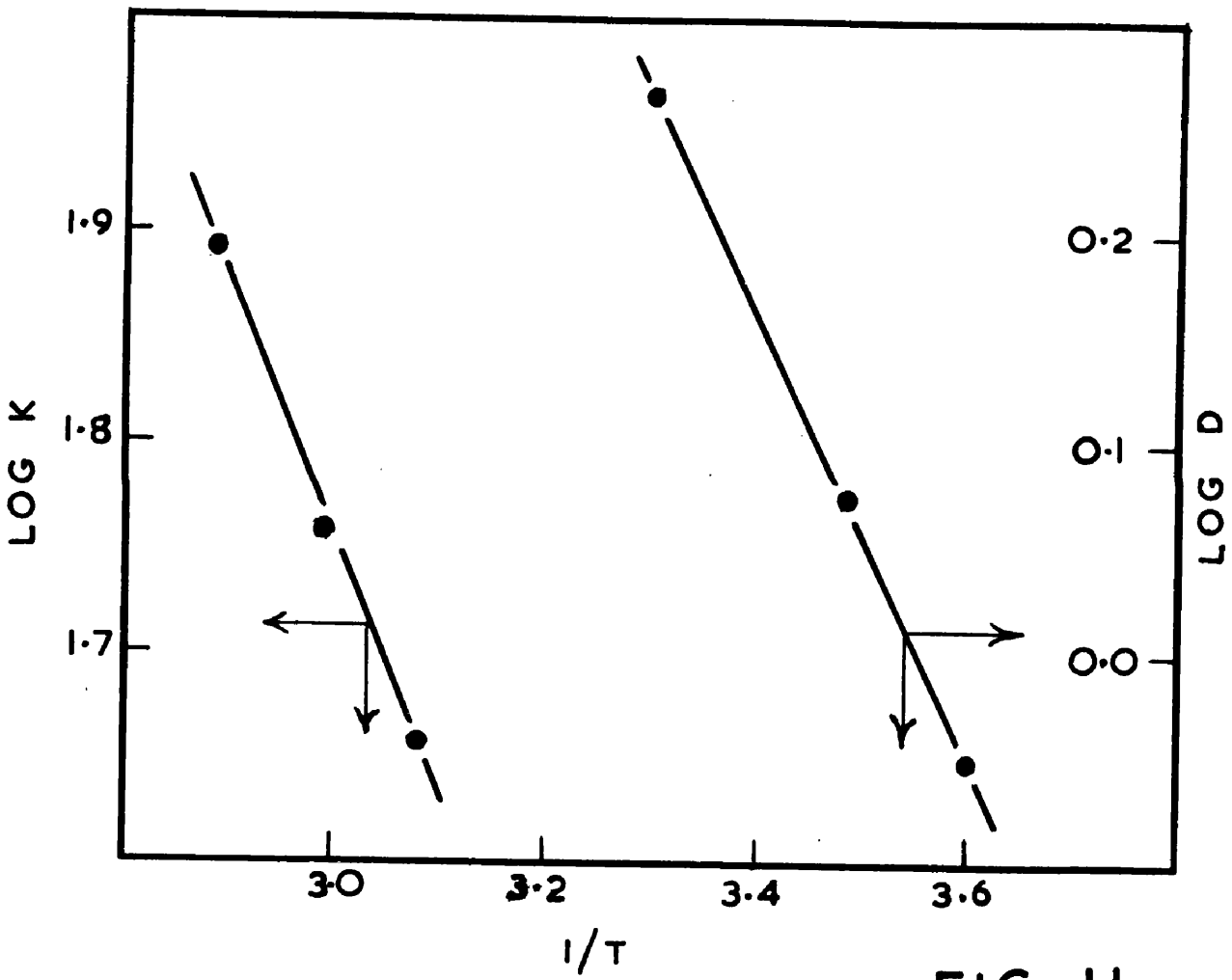


FIG. 11.

gives an activation energy for diffusion of 4.8 kilocalories per gm. mole. Van Hook[75] found that the activation energy for sucrose crystallisation decreased from 22kcals per gm. mole at 0°C to 6.5kcals per gm. mole at 70°C, and he believes that at the latter temperature the crystallisation of sucrose is a diffusion controlled process.

Wilhelm, Conklin, and Sauer[76] investigated the rate of solution of sodium chloride in water at 18°C, and found K to be of the order of 30 cms./hr. They assumed that the diffusivity remained constant from zero concentration to the saturation concentration and from the Berthoud relation that

$$K = \frac{D}{\delta}$$

calculated the film thickness through which diffusion took place to be 0.016 m.m.

The diffusion rate for sodium chloride in water is normally given as 1.35×10^{-5} cm.^{2}/sec. at 20°C. Making the assumption that $\frac{D\eta}{T}$ is constant, where η is the viscosity of the solution, values of D for other operating temperatures can be calculated, and hence the effective film thickness if diffusion controls crystallisation. The data are set out in Table 1 below, and show a constant value for the film thickness, comparable with that found for solution, which is

normally considered a diffusion controlled process.

Table 1 - Effective Film Thickness.

Temp. (°C)	D x 10^{8} (cm.^{2}/sec.)	K (cm./hr.)	Film Thickness (m.m.)
52	2.8	45.7	0.022
67	3.4	57.2	0.0215
73	4.3	77.4	0.020

By plotting mass transfer factor, Jd, versus modified Reynolds number, Chu, Kalil, and Wetteroth,[77] correlated the mass transfer data from many types of fluidised system. Using their correlation, and therefore treating crystallisation as a diffusional process, theoretical mass transfer coefficients have been calculated and are compared with the experimental values in Table 2. Agreement is not very good, but is perhaps as near as might be expected from such a wide basic relation.

Table 2 - Theoretical Mass Transfer Coefficients.

Temp. (°C)	Size of Crystal (mesh)	Soln. Velocity (cms./sec.)	K experimental) (cms./hr.)	K (theoretical) (cms./hr)
52	12-18	3	45.7	47.1
62	12-18	3	57.2	58.0
73	12-18	3	77.4	72.0
73	8-10	5	87.0	74.5

Summing up, the process of crystallisation at 52, 62 and 73°C has a similar activation energy as that for diffusion; the film thickness in crystallisation is of the same order as that present in solution; and the mass transfer coefficients calculated from dimensional correlation are of the same order as the experimental values. Crystallisation at these temperatures must therefore be controlled by diffusion and not by a surface reaction, at any rate for the range of supersaturation and crystal-solution relative velocity used in the experiments.

At lower temperatures than 52°C dependence of growth rate on supersaturation is more complex, and this suggests interference by surface alignment reactions. Such reactions may have a much higher temperature coefficient than the diffusion process. The conditions and duration of stirring to produce saturation were the same as at the higher temperatures, where the growth curves pass through the origin. The negligible rates of growth noted for supersaturation levels below 0.4 gms./litre may be due to some effective " energy barrier" or to temporary blockage of active growing areas by impurities in the solution. The critical supersaturation for growth is only 0.15% of the total solute present, and is therefore much smaller than the 50% required for surface nucleation as in the Volmer model.[47,55]

The dislocation theory, as proposed by Frank,[57] and Mott and Nabarro,[58] suggests that at low supersaturations the rate of growth will be proportional to the square of the supersaturation, and hence at very low supersaturations the rate of growth may be too small to measure. Also, a very small critical supersaturation may exist, since the critical two dimensional nucleus must be small enough to pass between dislocation centres.

The salt used in preparing both crystals and solution was an ordinary commercial product (Vacuum Salt) and the water was an ordinary Glasgow town water. The pH of the solution was 7.0 and it is not thought that any notable amount of impurity was present. However, Sears[66] has shown the inhibiting nature of adsorbed oxygen on the initiation of crystallisation from the vapour, and it is possible that traces of adsorbed impurity produce the same effect with sodium chloride.

Substances which are known to affect the crystallisation of sodium chloride are lead and cadmium ions,[65] urea[76], quaternary ammonium compounds,[79] and nitriloacetic acid.[80] McCartney and Alexander found that carboxymethylcellulose had notable effects on the crystallisation of calcium sulphate.[81] Small quantities of I.C.I. Cellofas B, the sodium salt of carboxymethyl-cellulose, were added to the solution to give a

concentration of 30 parts per million. This concentration had a very small effect on the viscosity (0.5% increase), and thence on the diffusion rates. As shown in Fig.12 the rate of crystallisation at 62°C was unaffected, but at 26 and 38°C, region of surface reaction control, the crystallisation rate drops sharply, with higher supersaturation levels before growth can be detected.

This supports the hypothesis that growth is diffusion controlled at high temperatures and surface reaction controlled at low temperatures.

Effect of solution velocity on the crystallisation rate.

The solution flow was increased from 3 cms./sec. to 5 cms./sec. through the empty fluidisation tube, and in addition 8-10 m.m. crystals (1.9 m.m.) were used at 73°C. Results are shown in Fig.13.

The crystallisation rate increased with solution flow both at 73 and 45°C. The increase in growth rate at 45°C was not expected (surface reaction control) and the increase in mass transfer coefficient at 73°C (Table 2), though relatively small, was more than expected, and shows a dependence of mass transfer on fluidising velocity to the power 0.43. This may have been caused by the relatively shallow beds used, and a wall effect from the one inch tube.

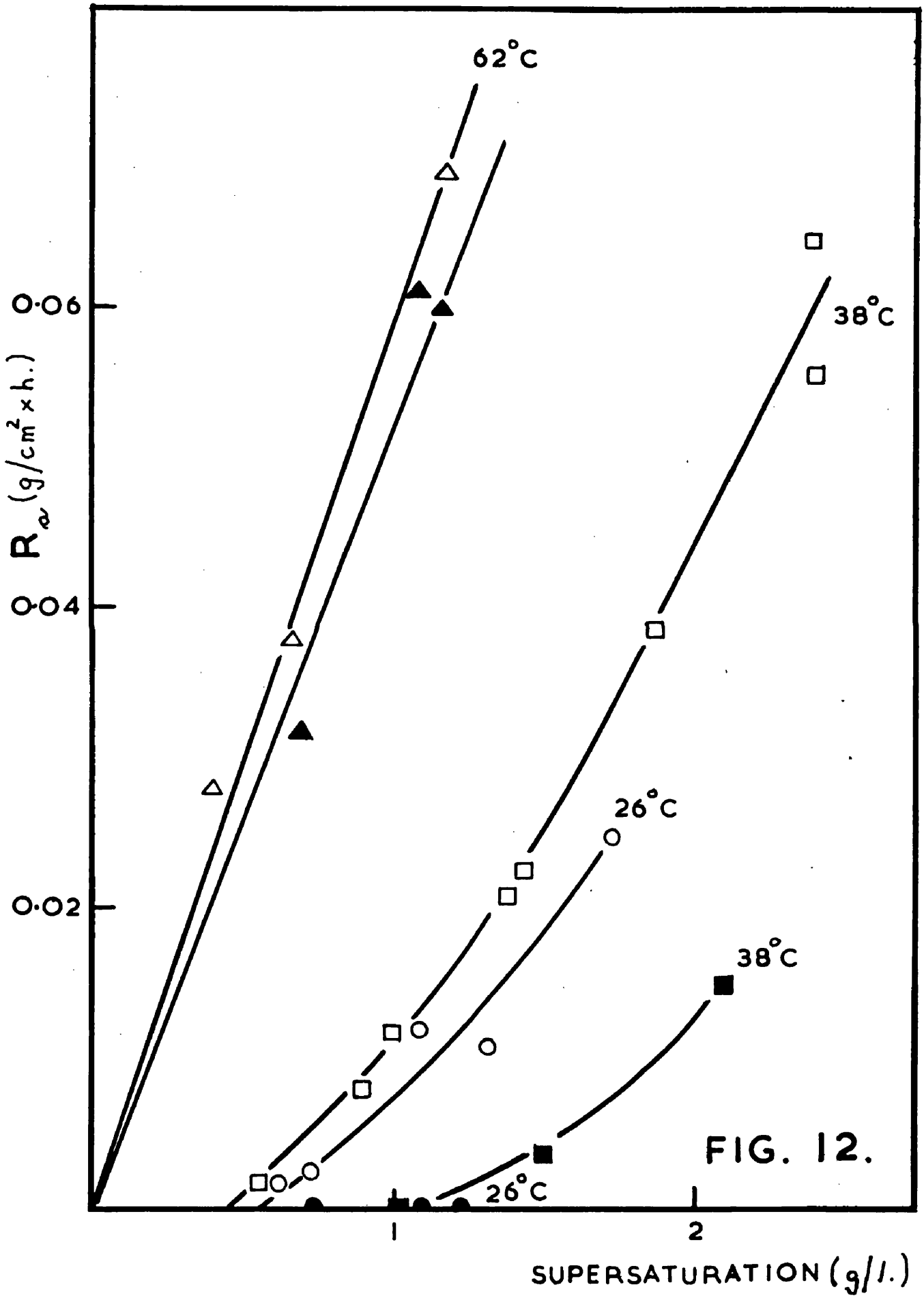


FIG. 12.

●,■,▲ – 30 P.P.M. CELLOFAS B

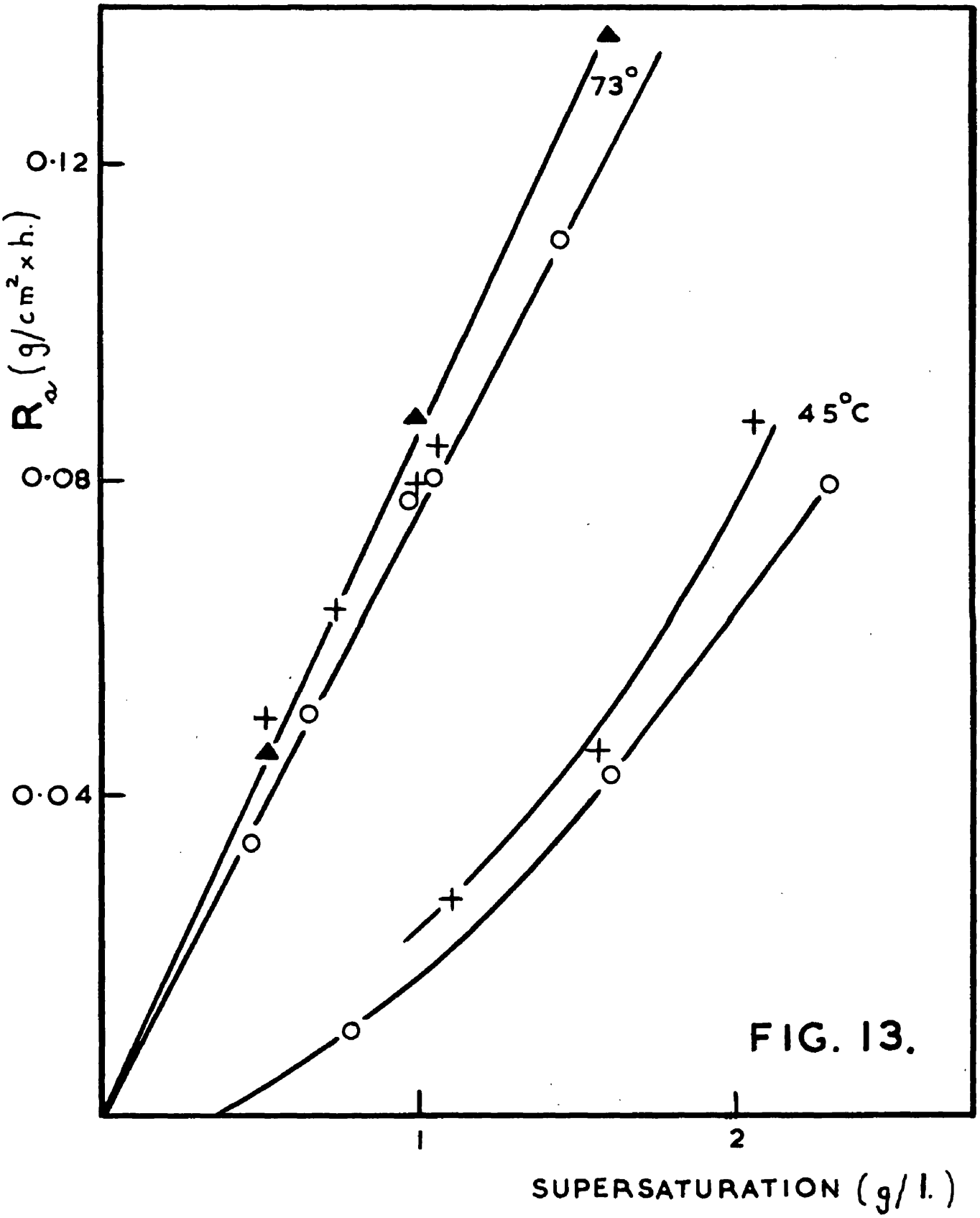


FIG. 13.

O — 12 - 18 MESH CRYSTALS, VELOCITY 3 CM/S.
+ — 12 - 18 " " " 5 "
▲ — 8 - 10 " " " 5 "

A fluidised bed is free to expand with the solution flow, so that the velocity past the crystal remains approximately constant up to the limiting velocity. Evans and Gerald[82] correlated fluidised bed mass transfer against modified Reynolds Number and concluded that the relationship between mass transfer coefficient, K, fluidising velocity, (V), and particle size (D_p), could be put in the form

$$K = \frac{c\, V^{0.33}}{(D_p)^{0.27}}$$

Bed densities at different fluidising velocities and various crystal sizes were determined, and the results are shown in Fig.14. The range of crystal sizes and fluidising velocities used in the experiments should cover all probable operational conditions. According to the Evan's relationship, the increase in mass transfer between the smallest crystals and the lowest fluidising velocity, and the largest crystals and the highest fluidising velocity, is only a factor of 1.6. Provided the crystal bed is adequately fluidised, solution velocity and crystal size make little difference to growth rate. A similar result has been obtained for mass transfer from particles in stirred vessels.[83] Once the stirrer speed is sufficient to suspend the particles, increase in stirrer speed makes little difference to the rate of mass transfer.

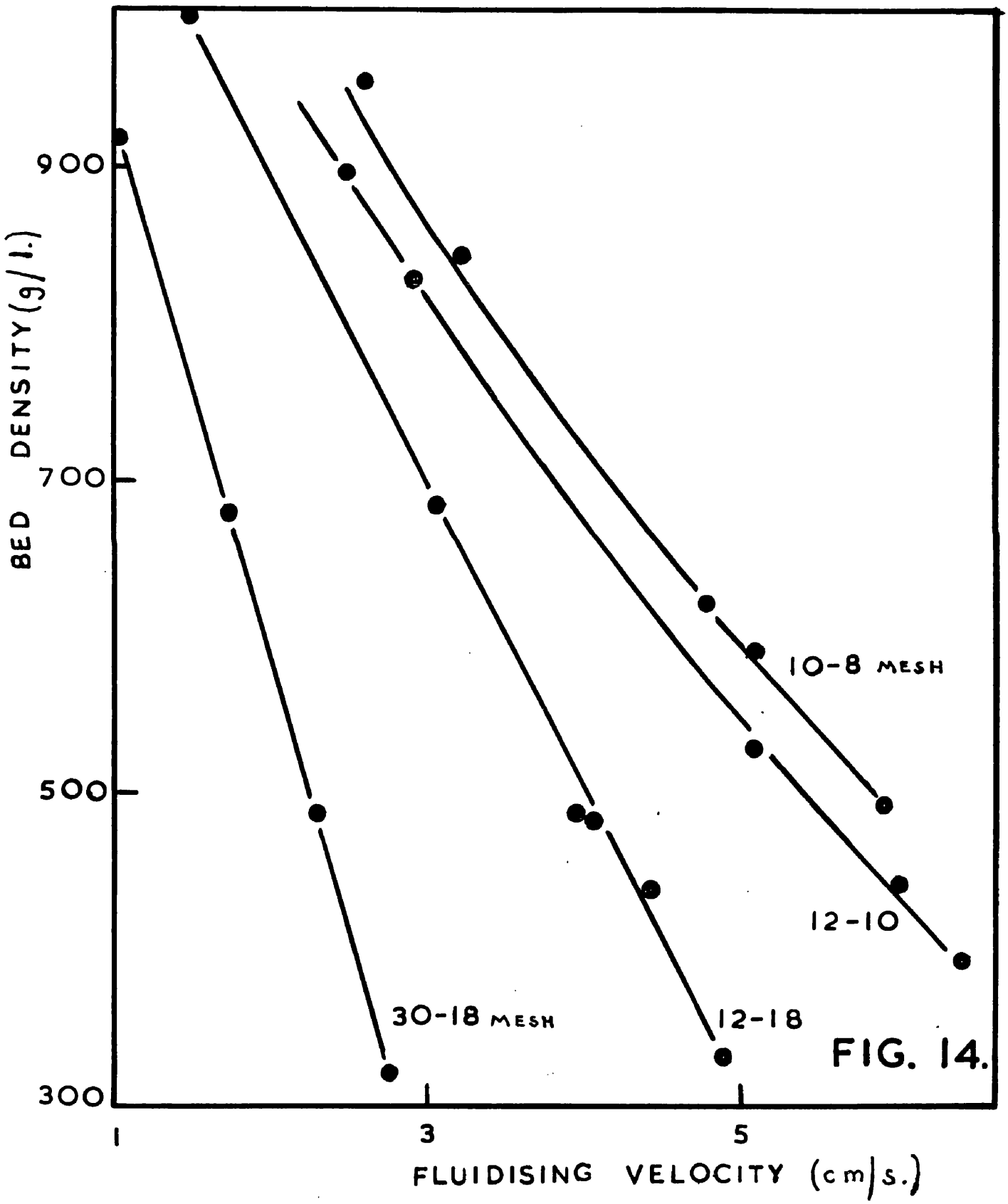

900
700
500
300
BED DENSITY (g/l.)
1
3
5
FLUIDISING VELOCITY (cm/s.)
10-8 MESH
12-10
12-18
30-18 MESH

FIG. 14.

Effect of growth rate on crystal quality.

At rates of growth higher than 0.07 gms./cm.^{2} x hr. it was noted that the crystal surface was irregular, and studded by small excrescences. Microscopic examination showed these to be small cubes - the solution was in effect depositing fresh nuclei at the existing surface. The new growth could readily be removed by attrition, and would then behave as a freshly detached nucleus.

1b. Continuous crystallisation in the laboratory crystalliser.

Effect of production rate on fines formation.

The crystalliser was worked as an evaporator, and the solution temperature was kept constant at 38°C. Commencing with a standard weight of either 100 or 200 gms. of 12-18 mesh (1.1 m.m.) crystals as the initial bed, the heating water temperature was varied to give deposition rates of from 25-100 gms./hr. in the crystalliser. Each run was continued for one hour.

The fines separator removed all, or nearly all, the solid fragments carried out of the suspension. These were about 0.1 m.m. size, and were removed at the end of the run, filtered, washed with methanol, dried and weighed.

The results are shown in Fig.15. The ratio of weight of fines (F) to weight of crystal (P) deposited

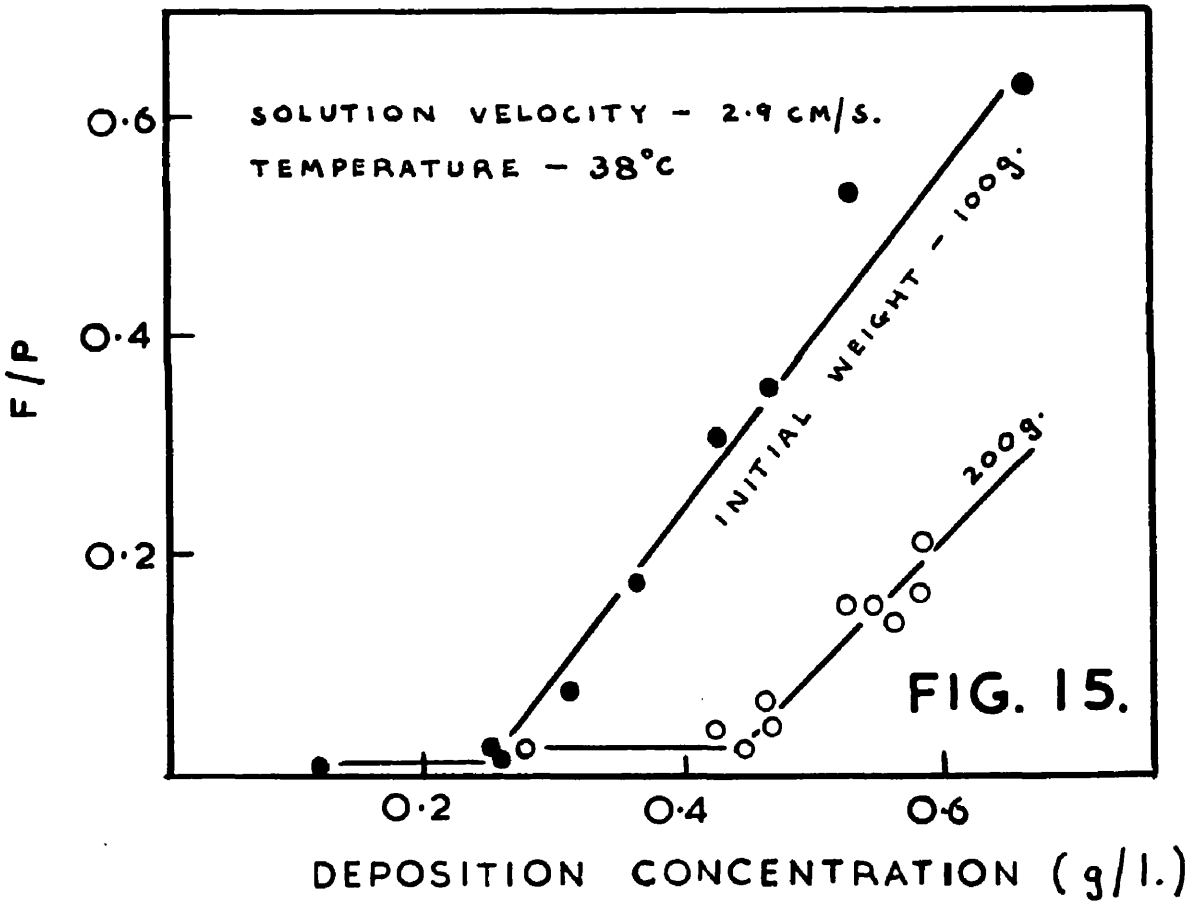

SOLUTION VELOCITY - 2·9 CM/S.
TEMPERATURE - 38°C
INITIAL WEIGHT - 100g.
200g.
F/P
0·6
0·4
0·2
0·2
0·4
0·6
DEPOSITION CONCENTRATION (g/l.)

FIG. 15.

on the seed crystals has been plotted against the deposition concentration, which is the total salt deposited per hour divided by the solution flow per hour, and must also be the amount whereby the inlet concentration exceeds the outlet.

The curves show a sharp upturn when some limiting value of deposition concentration is reached. This limiting value is 0.25 gms./litre, equivalent to a production rate of 52 gms./hr. with an intial seed load of 100 gms. This rises to 0.43 gms./litre, equivalent to a production rate of 83 gms./hr. with an initial seed load of 200 gms.

Now the crystallisation process was continuous and the supersaturation could increase cyclically until either the supersaturation was high enough to force the required amount of crystallisation on the available crystal surface, or until the metastable limit was reached, when nucleation resulted, with the formation of fresh crystal surface.

Samples were taken after 30 minutes from the supersaturated solution in the downtake when the crystalliser was operating at a production rate of 50 gms./ hr. with 100 gms. initial seed weight. The fines produced at this rate were negligible. The samples were analysed for total chloride present using silver nitrate, and potassium chromate as an indicator, and the

actual supersaturation was found to be 1.5 gms./litre. Increased production rate meant increasing supersaturation and nucleation. Therefore the "metastable limit" for sodium chloride solutions under boiling conditions must be about 1.5 gms./litre.

The logarithmic mean supersaturation, calculated from the inlet supersaturation of 1.5 gms./litre and the "deposition concentration" of 0.25 gms./litre, is 1.38 gms./litre (log. mean of 1.5 and 1.25 gms./litre). 52 gms. of solute were deposited on 2,720 sq. cms. of crystal surface giving a growth rate of 0.019 gms./ $cm.^2$ x hr. From the cooling batch crystalliser the growth rate is 0.021 gms./ $cm.^2$ x hr., at 1.38 gms./ litre at 38°C.

Similarly at 83 gms./hr production rate and with 200 gms. initial seed weight the log. mean supersaturation is 1.28 gms./litre and the growth rate is 0.016 gms./ $cm.^2$ x hr., and the equivalent growth rate from the cooling crystalliser is 0.0185 gms./ $cm.^2$ x hr.

Considering the inaccuracy in measuring the very small metastable supersaturation, and the time delay in the continuous crystalliser increasing cyclically from the deposition concentration to the equilibrium concentration value, there is a satisfactory agreement between the rates of growth from the two crystallisers operating under different conditions.

The rate of growth of the seed crystals was calculated for each run, and the active supersaturation to produce this rate of growth was extrapolated from the cooling crystalliser results. The inlet supersaturation was calculated from the active supersaturation and the deposition concentration, and the inlet supersaturation for each run is plotted against the weight of fines produced in Fig.16. The results for the 100 and 200 gms. initial bed weight fall fairly close together, and show the metastable limit to be 1.5 gms./litre as found by direct titration.

After the solution passed through the bed the supersaturation was reduced below the level where rapid nucleation takes place. Therefore the nucleation properties of the system must have been similar to those occurring in crystal beds deep enough to reduce the exit supersaturation to negligible proportions. In these circumstances the total crystal production can be calculated, and the fine crystal which will be expected is shown, and calculated as a percentage of the total crystal " make" in Table 3. The weights are for a crystalliser of the same dimensions as the experimental unit, but the percentage fines should be valid for all production units.

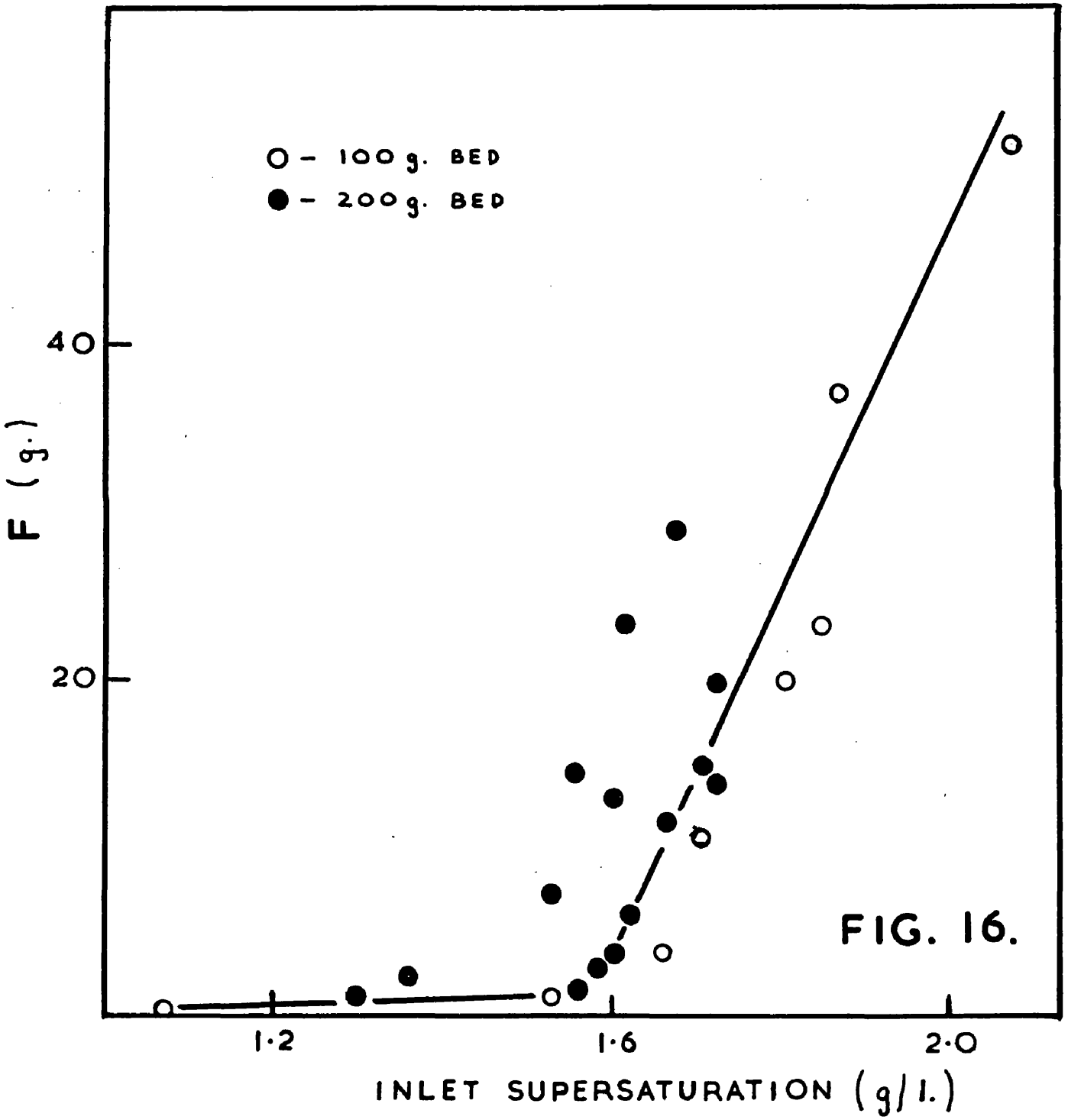


FIG. 16.

Table 3 - Percentage Fines Produced

Inlet supersatn. (gms./l.)	Total prodn. (gms.)	Fines (gms.)	Product crystals (gms.)	% Fines
1.4	294	1.5	292.5	0.5
1.5	314	3.0	311	1.0
1.6	336	7.0	329	2.1
1.7	357	15.0	342	4.2
1.8	378	26.0	352	6.9
1.9	400	38.0	362	9.5
2.0	420	50.0	370	11.9

A personal communication from I.C.I. Salt Division states that a fines fraction of 11% is obtained from full scale Oslo crystallisers when they are operating at an inlet supersation of 2.2 gms./litre. Part of the fines fraction will also be removed as product in the I.C.I. crystalliser, and the agreement is therefbre good.

Effect of crystal bed weight.

In another series of tests the deposition concentration was held constant at 0.64 gms./litre, and the initial seed weight steadily decreased, with a resulting steady increase in the ratio of the weight of fines to the solute deposited on the crystals. In Fig.17 the ratio $\frac{F}{P}$ is plotted against the ratio of solute crystallised to the average weight of crystals present in the bed during the run ,

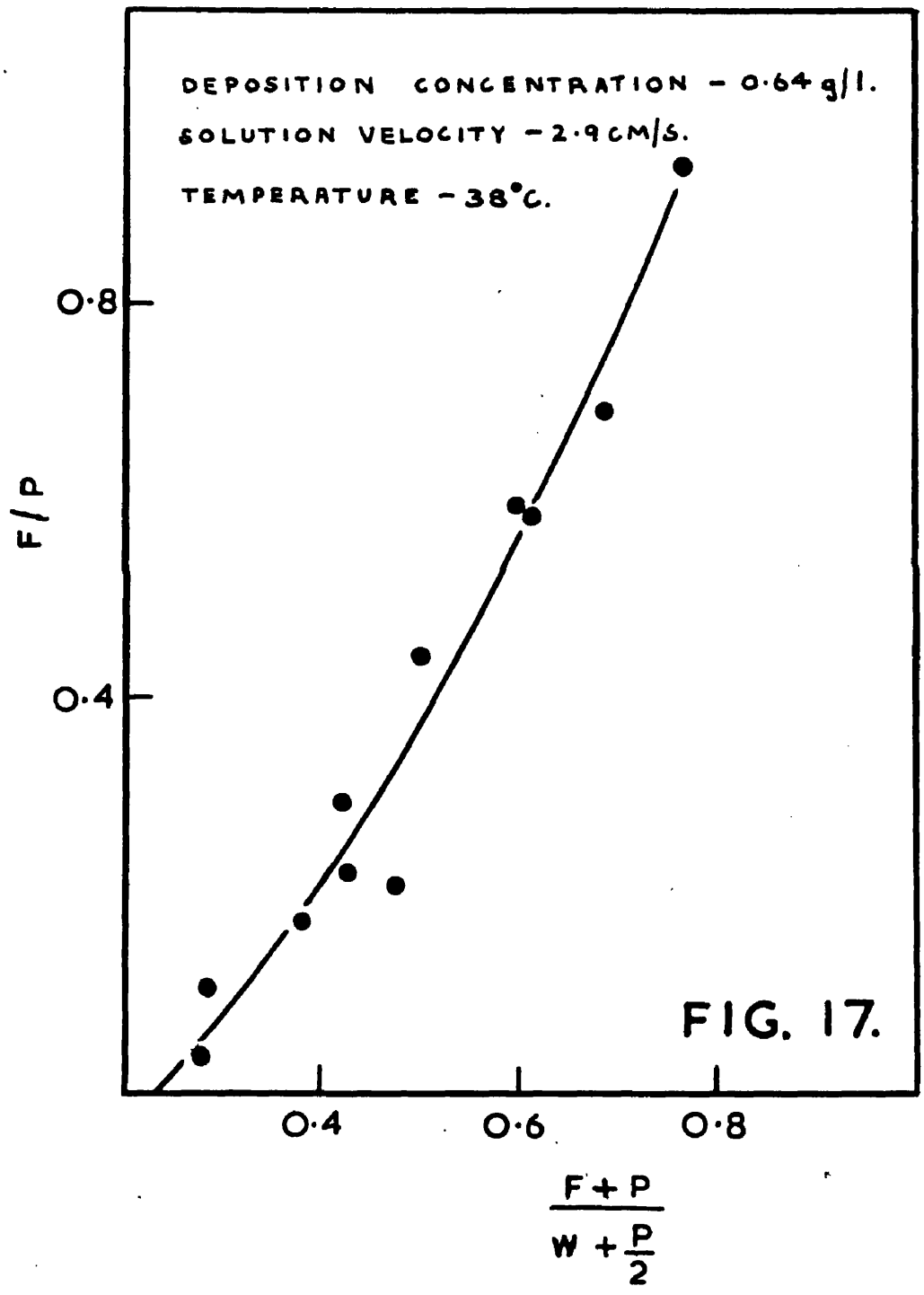

DEPOSITION CONCENTRATION - 0·64 g/l.
SOLUTION VELOCITY - 2·9 CM/S.
TEMPERATURE - 38°C.
0·8
0·4
F/P
0·4
0·6
0·8
F + P
W + P/2

FIG. 17.

$$\frac{F + P}{W + \frac{P}{2}}$$

Continuous production.

With the fines separator removed from the system product crystals were removed continuously from the base of the crystalliser. The deposition concentration was 0.24 gms./litre; the bed was 19 ins. deep and contained 950 gms. of crystals; and product crystals were removed at the rate of 50 gms./hr. When equilibrium conditions had been reached the product crystals had the weight composition shown in Table 4.

Table 4 - Weight Composition of Product Crystals at Equilibrium.

Crystal size.	% by weight
8-10 mesh	70.1
10-12 "	28.8
12-18 "	1.1

The product crystals were cubes with the corners and edges rounded by abrasion, the larger crystals being relatively more rounded. They were not spherulites, and cleavage exposed hard shiny surfaces. A sample is shown in Fig.18 compared with vacuum pan sodium chloride crystals. Fig.19 is an X-ray rotation

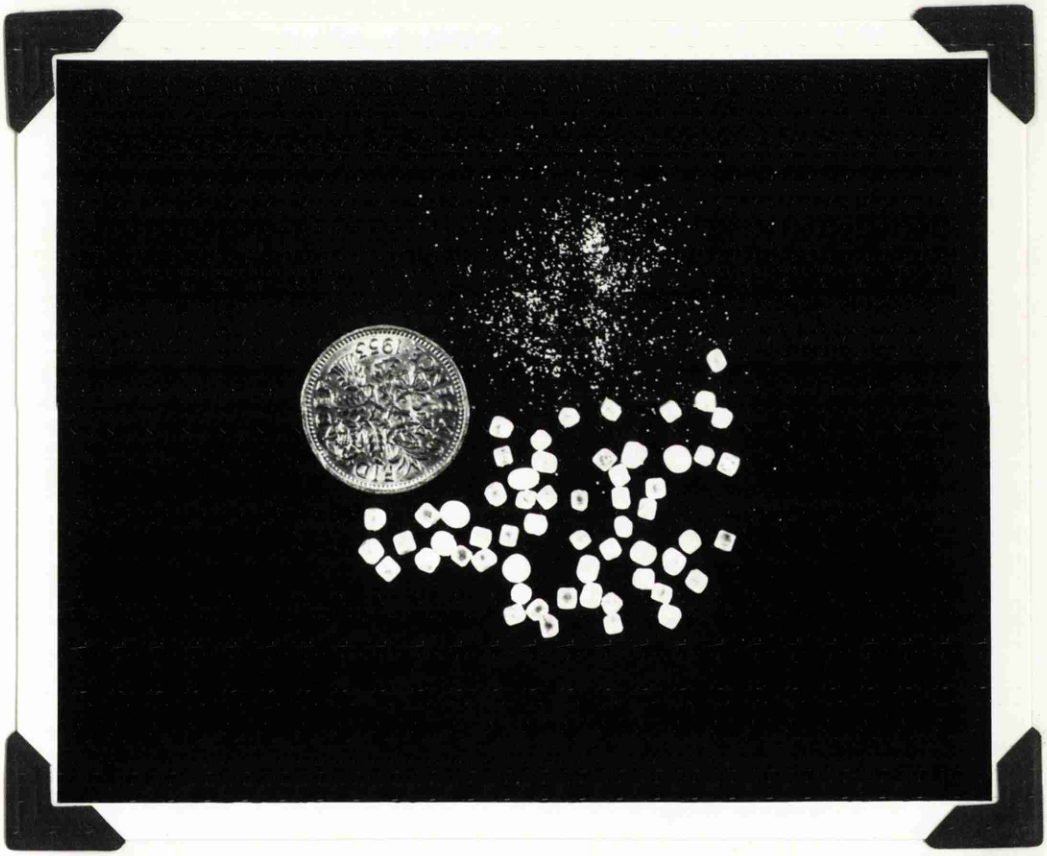


Figure 18. Sodium chloride product crystals compared with 'Vacuum Salt'.

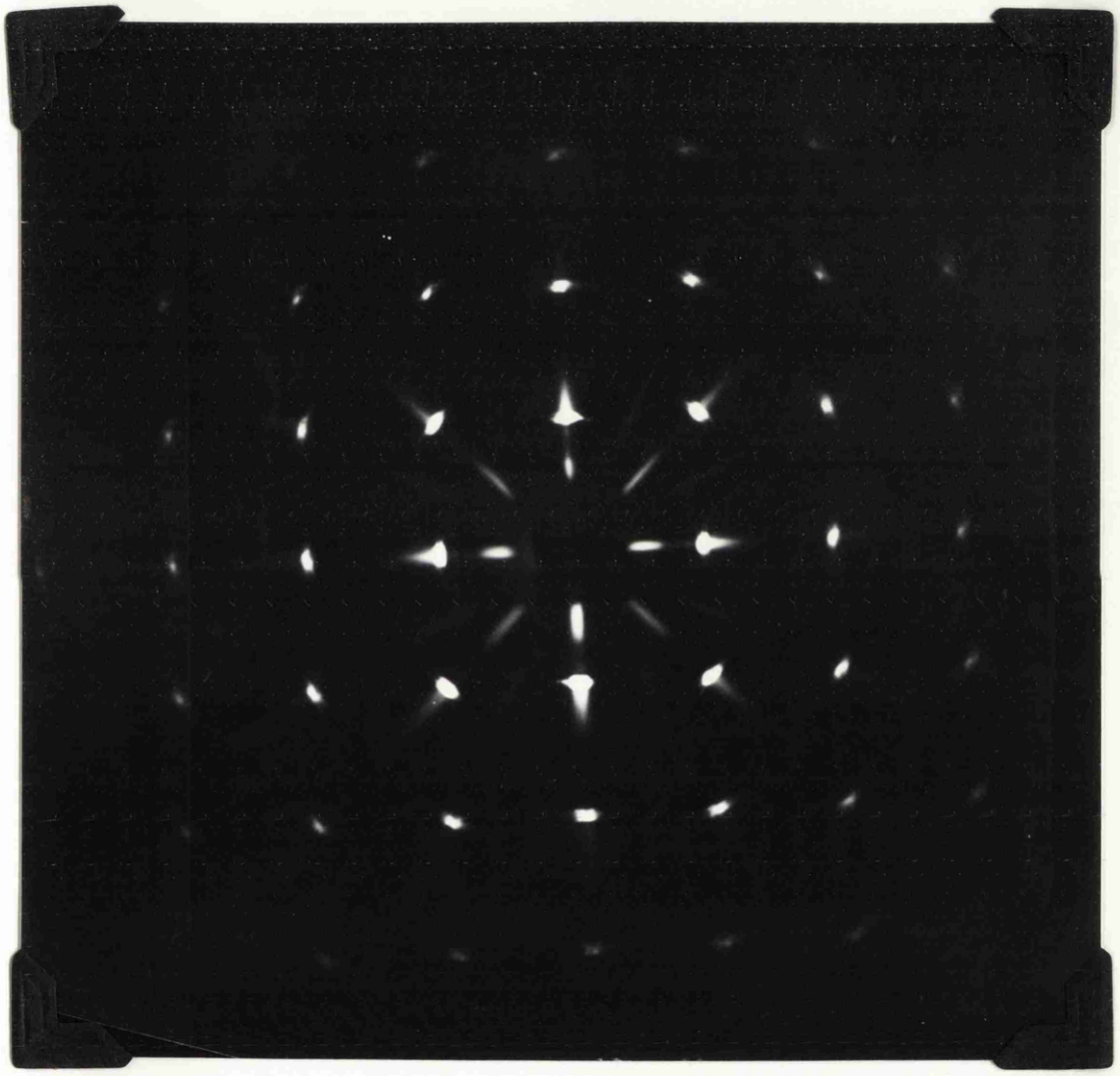


Figure 19. X-ray rotation photograph of product crystal.

photograph of a single product crystal, and shows the typical pattern of a cubic structure. A spherulitic, or poorly formed mosaic crystal would not have given such an even pattern.

At this low rate of production relative to weight in the suspended bed, supersaturation was largely discharged in passage through the crystalliser. Growth rates were about one-tenth of those measured with the 100 gms. mass, and effective supersaturation was correspondingly lower. This point will be discussed later.

1c. Crystallisation in the semi-technical plant.

95 lbs. of 10-12 mesh (1.4-1.6 m.m.) crystals were tipped as a slurry into the crystalliser to give a fluidised bed 2-3 ft. deep. This bed was retained in the glass vessel during the crystallisation, and only a few fine crystals circulated with the solution.

The production rate was varied between 8 and 33 lbs/hr. by alteration in heater conditions, and the operating temperature was 73°C.

The size of the product crystals, the inlet supersaturation to the bed, the production rates, and the total weight of salt produced are given in Table 5.

Table 5 - Product of Salt Crystals by Semi-technical Plant.

Inlet Supersat. (gms./l)	Total Prodn. (lbs.)	Prodn. rate (lbs./hr.)	% by weight +10 mesh	10-12 mesh	12-18 mesh	18-30 mesh	-30 mesh
0.4	171	8	54.5	25	17	2.6	0.9
0.6	69	13	54.5	24.5	20	1.0	0.0
1.0	139	20	85.5	8.0	1.2	0.0	4.3
1.6	100	32	50.2	32.0	15.8	1.5	0.5

Long operational runs on a large plant are difficult to perform in a College because of shortage of labour and limited service, and therefore experimental runs are too short. The ratio of crystal " make" to crystal in the fluidised bed should be as high as possible, and certainly greater than was attained in these tests. At the same time, the suspended mass was discharged at the end of the run and screened. The size distribution was very close to that of the withdrawn product except for a higher proportion of -30 mesh material. The results were, however, consistent with those obtained in the laboratory tests as will be seen below.

At a production rate of 32 lbs./hr. the mean retention time for a bed weight of 96 lbs. is 3 hrs., while the dominant crystal size is about 2 m.m.. Saeman has shown (Section 2d above) that the dominant crystal size must be based on a retention time of three times the mean retention time based on weight, and hence the

2 m.m. crystals took 9 hrs. to grow. This suggests a linear growth rate of 0.22 m.m./hr. or 0.024 gms./cm.^{2} x hr. From Fig.9 this is seen to be equivalent to an effective supersaturation of 0.3 gms./litre. As the inlet supersaturation is 1.6 gms./litre, the outlet supersaturation, based on log. mean calculations, is 8×10^{-3} gms./litre. With such small outlet levels the great bulk of crystal growth will take place around the liquid inlet, as Saeman and Miller noted for ammonium nitrate.[2]

It would follow from this that the output of sodium chloride crystals from an Oslo crystalliser operating at 73°C will be almost independent of bed depth, and can be expressed as output per square foot of crystalliser cross sectional area.

When the inlet supersaturation of 1.6 gms./litre was exceeded in an attempt to increase production, notable nucleation occurred, as might be expected from the tests with the laboratory unit. Even at a rate of 32 lbs/hr., with the limiting inlet concentration, there was some deposition of crystal at any irregularity in the downtake pipe or flashhead.

The crystal quality was always excellent when a proper bed of large crystals was present, but irregular masses of aggregates sometimes appeared when appreciable quantities of fines were circulating with the brine.

It was noted that the top 20% of the crystal bed seemed to form a partly classified section of smaller crystals, with the remaining 80% of large crystals evenly mixed and uniform.

No cubic hillocks were observed on the crystal surface as were found at growth rates greater than 0.07 gms./cm.^{2} x hr. in the operation of the batch cooling crystalliser. This freedom from poor growth was probably caused by the mixing of the large bed preventing crystals from staying in the region of high supersaturation at the base of the crystalliser, but carrying them away to zones of lower supersaturation. Indeed this was the method used by Miller and Saeman[2] to avoid poor crystal growth formation with ammonium nitrate.

It was noted that the larger the crystals, the more rounded they became. Crystals of 1 m.m. size were perfect cubes, and crystals above 2 m.m. size were almost spherical. Crystals in the batch crystalliser always retained their cubical habit whether the supersaturation was high or low. The rounding of the crystal must have been caused by attrition of the larger crystals in the rapidly moving mixed section of the bed, whereas the crystals under 1 m.m. size suffered little attrition in the gently fluidised classified section. Since the growth rate of sodium chloride is

high, a relatively shallow crystal bed is possible, and a bed height of, say 10 ft., will increase the effect of attrition, giving a spherical product, without increasing the total growth.

The fact that the rounded crystals were produced by attrition suggests that growth is diffusion controlled as already stated. There was no tendency to replace corners and edges to reform a cube, and the sphere is the form which should be adopted if crystal growth is anisotropic. On the other hand, sodium thiosulphate, which shows some measure of surface reaction control, always retains its sharp corners and edges, under similar conditions of attrition.

In general operation of the plant it was found to be impracticable to start with a saturated solution and evaporate until nucleation occurred. A milky white suspension containing a very large number of nuclei was formed, and could flow through the plant for days before sufficient large crystals were obtained to form a proper fluidised bed. The operating procedure was to take screened vacuum salt of 0.2-0.5 m.m. size as the original seed, and to form a bed from this by slow growth and crystal removal. Ideally the plant should be restarted with a bed of full size crystals to enable size equilibrium to be attained quickly. When small seed crystals are used to start the bed, the crystals

pass through a stage of poor quality. The small crystals tend to cluster together to form a larger, easily fractured, opaque crystal of 1 m.m. size, which must be removed from the bed before good, clean crystals appear as product.

Flash nucleation must be avoided after seeding, and this restricts supersaturation to below 1.6 gms./litre under normal operating conditions, unless a fines separator is in constant use. Any industrial scale Oslo crystalliser should have a fines separator to destroy excess nuclei which may be formed by control fluctuations.

As the velocity of solution circulation is also limited by the need for proper fluidisation, it follows that any industrial sodium chloride crystalliser has some limiting output which can be expressed in e.g. pounds/square foot of crystalliser cross sectional area.

1d. Conclusions.

The crystal growth of sodium chloride can be controlled by fluid diffusion (above 50°C) or by surface orientation (below 50°C).

Mass transfer coefficients of the order of 80 cms./hr. can be obtained in a fluidised bed of 1-2 m.m. size crystals.

For controlled crystal growth, supersaturation must not exceed 1.6 gms./litre, and the ratio of hourly production weight to bed weight should not exceed 1 to 3. A fines separator should be built into industrial units to destroy any excess nuclei which may be formed.

The limiting output of a sodium chloride crystalliser producing 2 m.m. crystals is 40 lbs/ft.^{2} of crystalliser cross sectional area.

Mixing of the fluidised bed prevents poor growth at high supersaturation levels.

The larger the product crystal the more spherical it becomes.

An Oslo crystalliser should preferably be put into operation with a bed of full sized crystals in the suspension holder.

Results are consistent from a small laboratory scale up to a 12 ins. diameter crystalliser, but further experiment is required over a longer period for latter tests.

The general results from this section on Sodium Chloride Crystallisation were summarised in a paper presented to the Institution of Chemical Engineers (London Section) in October, 1959. (Bain and Rumford, Trans. Instn. Chem. Eng., 1960, 38, 10).

2. The Crystallisation of Hydrated Sodium Thiosulphate (Hypo).

It is difficult to produce sodium chloride as a large grained crystal, and therefore "hypo" was chosen as a solute because its ease of crystallisation to give large crystals gave a comparison between extremes. It is also characteristic of the solid hydrate crystal type as compared to the anhydrous sodium chloride. Hypo is colourless, and in agitated solution crystallises as beautifully formed monoclinic prisms. The industrial "pea" crystals are some 5 m.m. in size. The temperature coefficient of solubility is high, and the salt melts in its own water of crystallisation at 48°C.

2a. Cooling crystalliser experiments.

Operational proceedure was similar to that given for sodium chloride, except that the duration of each run was 12 minutes. The crystals and solution used in the experiments were prepared from pea crystals of commercial "hypo" and Glasgow tap water, and the experimental crystals were prepared in the laboratory Oslo crystalliser.

The surface area of the crystals was estimated by deriving an experimental constant c in the equation

$$W = c\ A^{\frac{3}{2}}$$

where W is the weight of the crystal and A is the surface area of the crystal. The dimensions of 50

large crystals (6 m.m.) were measured microscopically and the surface area calculated. The constant c was found to be 0.136 gms/cm.$^{\frac{3}{2}}$

The same assumptions for active supersaturation and crystal surface area were made as for sodium chloride. Solubility data were taken from the I.C.T. (1st Edn., Vol.4, p.232) and solution densities from the work of Butler.[3]

Rate of crystal growth.

Fig.20 shows the effect of supersaturation, expressed in gms. of supersaturated solute (sodium thiosulphate pentahydrate) per litre of solution, on the rate of crystal growth, in gms. of solute deposited per hour, per square centimetre of crystal surface.

Crystallisation was carried out at 24, 30, 35 and 40°C. The crystals used were 6→10 mesh (2→3 m.m.), and the solution velocity through the empty crystallisation tube was 2.7 cms./sec.

At 30, 35, and 40°C, the rate of growth is linear with respect to supersaturation, and temperature has no effect on the crystallisation rate. At 24°C the rate of growth is slower and more random than at the other temperatures.

The mass transfer coefficient is 4.3 gms./cm.^{2} x hr. x gm./c.c. (4.3 cms./hr.), which is about one-tenth of the value found for sodium chloride. Butler[3] measured

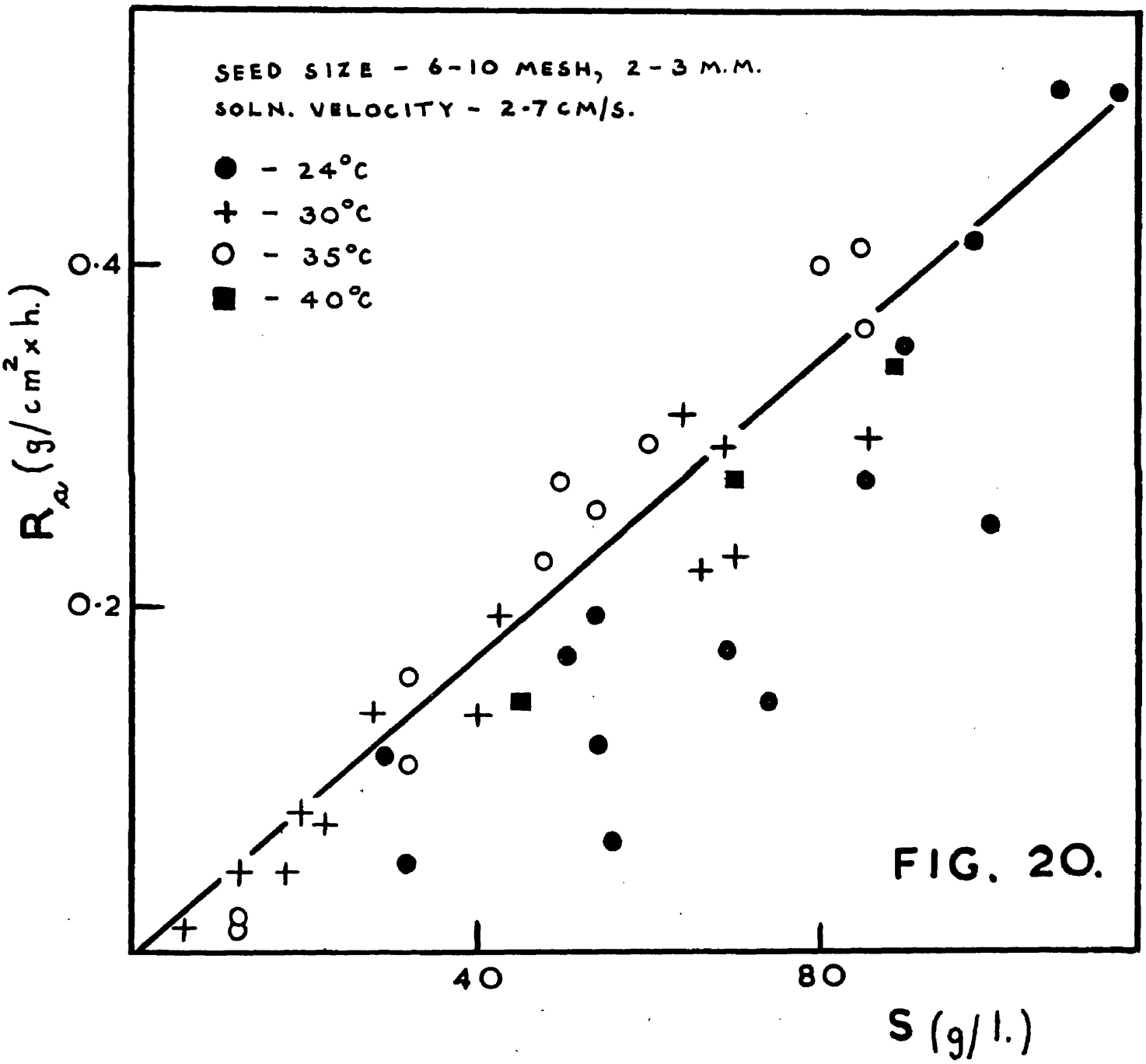

SEED SIZE - 6-10 MESH, 2-3 M.M.
SOLN. VELOCITY - 2-7 CM/S.
● - 24°C
+ - 30°C
○ - 35°C
■ - 40°C
0·4
0·2
R_α (g/cm² x h.)
+ 8
40
80
S (g/l.)

FIG. 20.

the linear rate of growth of large single crystals of hypo rotating in supersaturated solution. When Butler's results are recalculated to give a mass transfer coefficient, it is found to be 0.82 gms./ cm.^{2} x hr.x gm./c.c.

In Fig.21 the ratio of supersaturated concentration to saturated concentration is expressed as a percentage, and plotted against the rate of growth. The effect of this is to accentuate the disparity between growth rate at 24°C and the rates at higher temperatures, which show no increase in growth rate with temperature.

Butler also found no increase in growth rate with temperature.

Fig.22 shows the effect of supersaturation on growth rate for 6→7 m.m. crystals at a somewhat higher solution velocity of 3.9 cms./ sec. The growth rates at 30 and 40°C lie together, while the rates of growth at 24°C are slightly lower.

Effect of crystal size and fluidising velocity.

The experiments illustrated in Fig.23 show that an increase in solution velocity and crystal size gives slightly higher growth rate, though these are not proportional to the product of the variables. As the crystal bed is not static but tends to expand in the normal way of fluidising, this is not surprising.

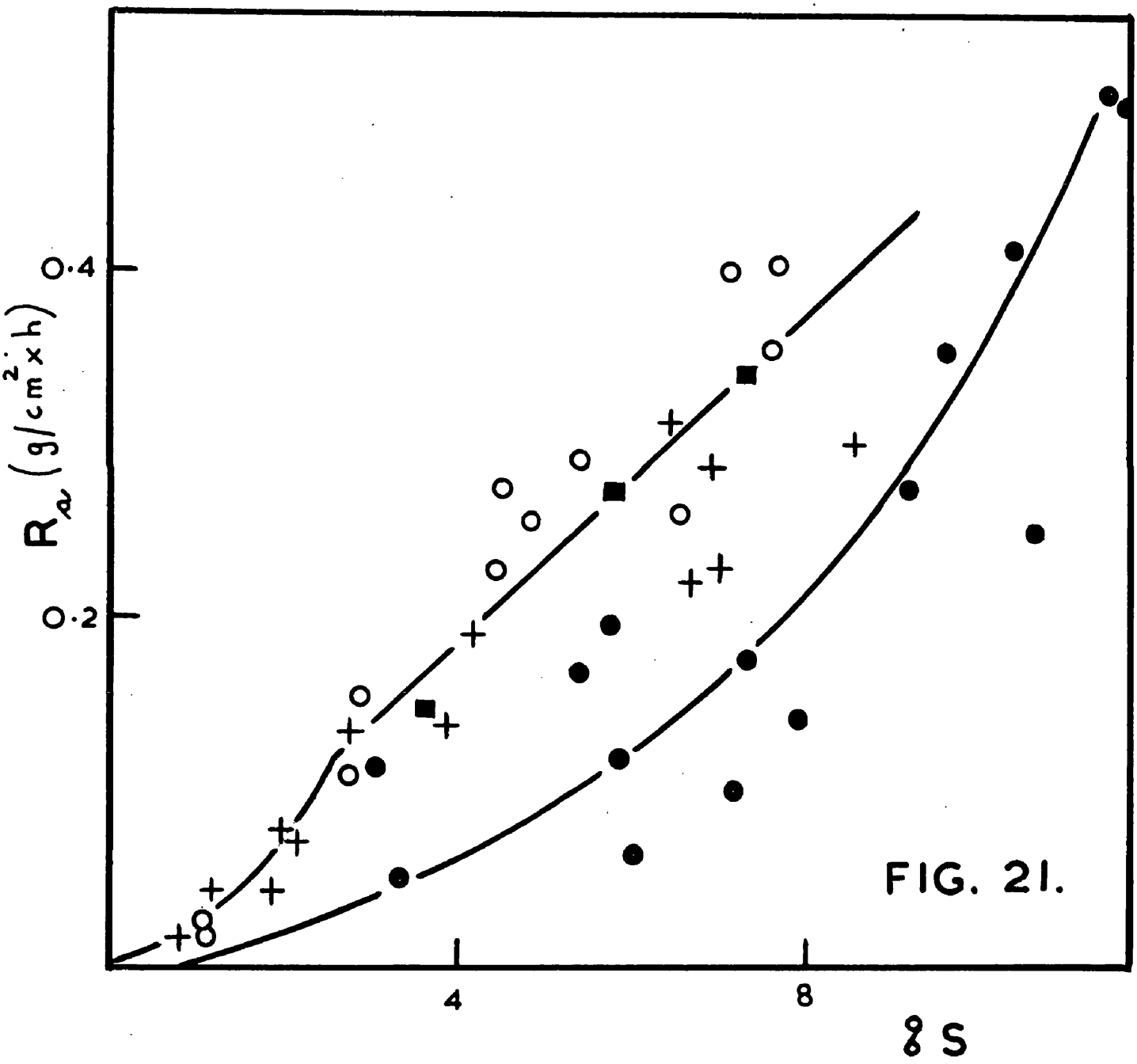


FIG. 21.

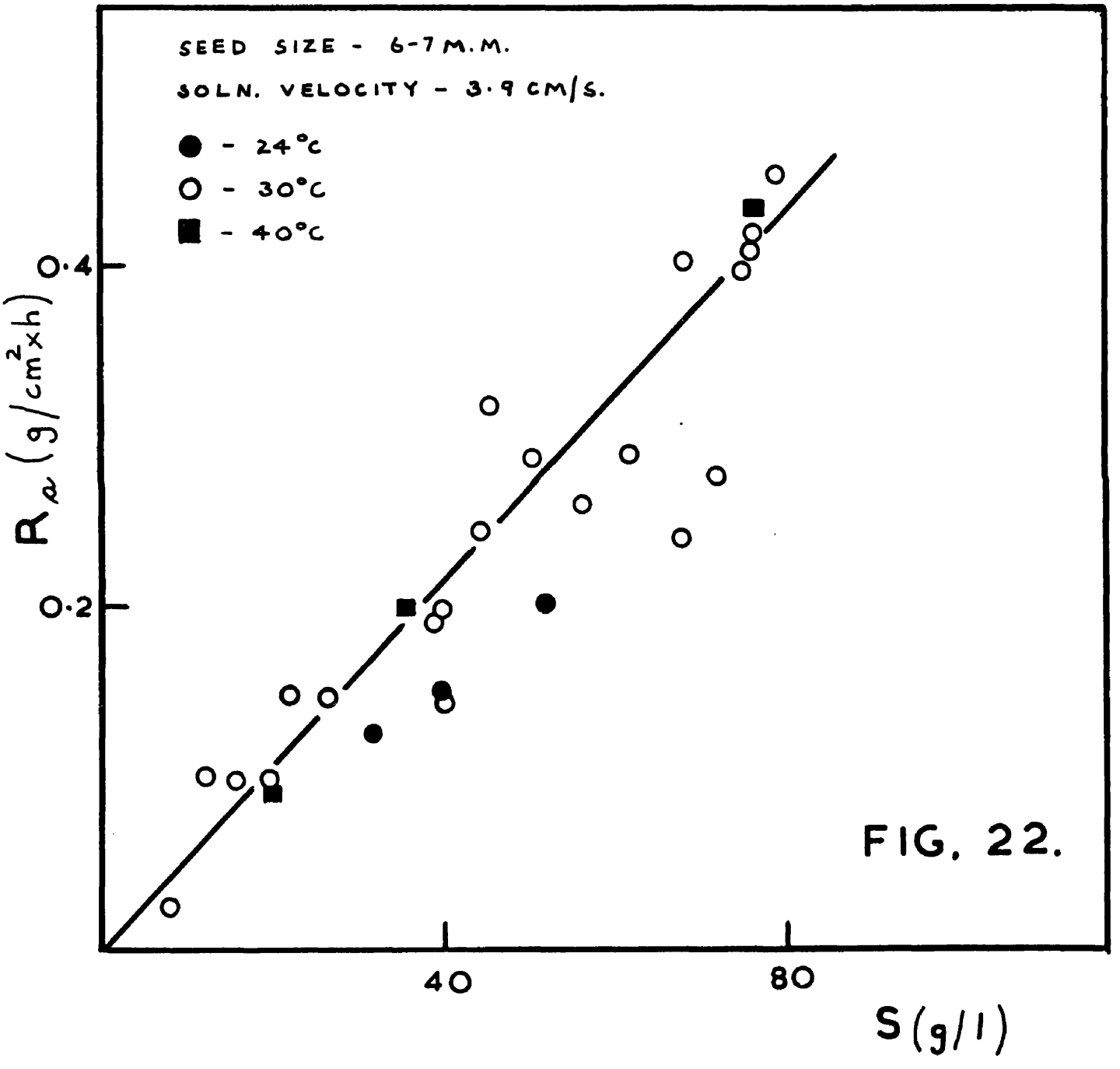

SEED SIZE - 6-7 M.M.
SOLN. VELOCITY - 3·9 CM/S.
● - 24°C
○ - 30°C
■ - 40°C
0·4
0·2
R_a (g/cm²xh)
40
80
S (g/l)

FIG. 22.

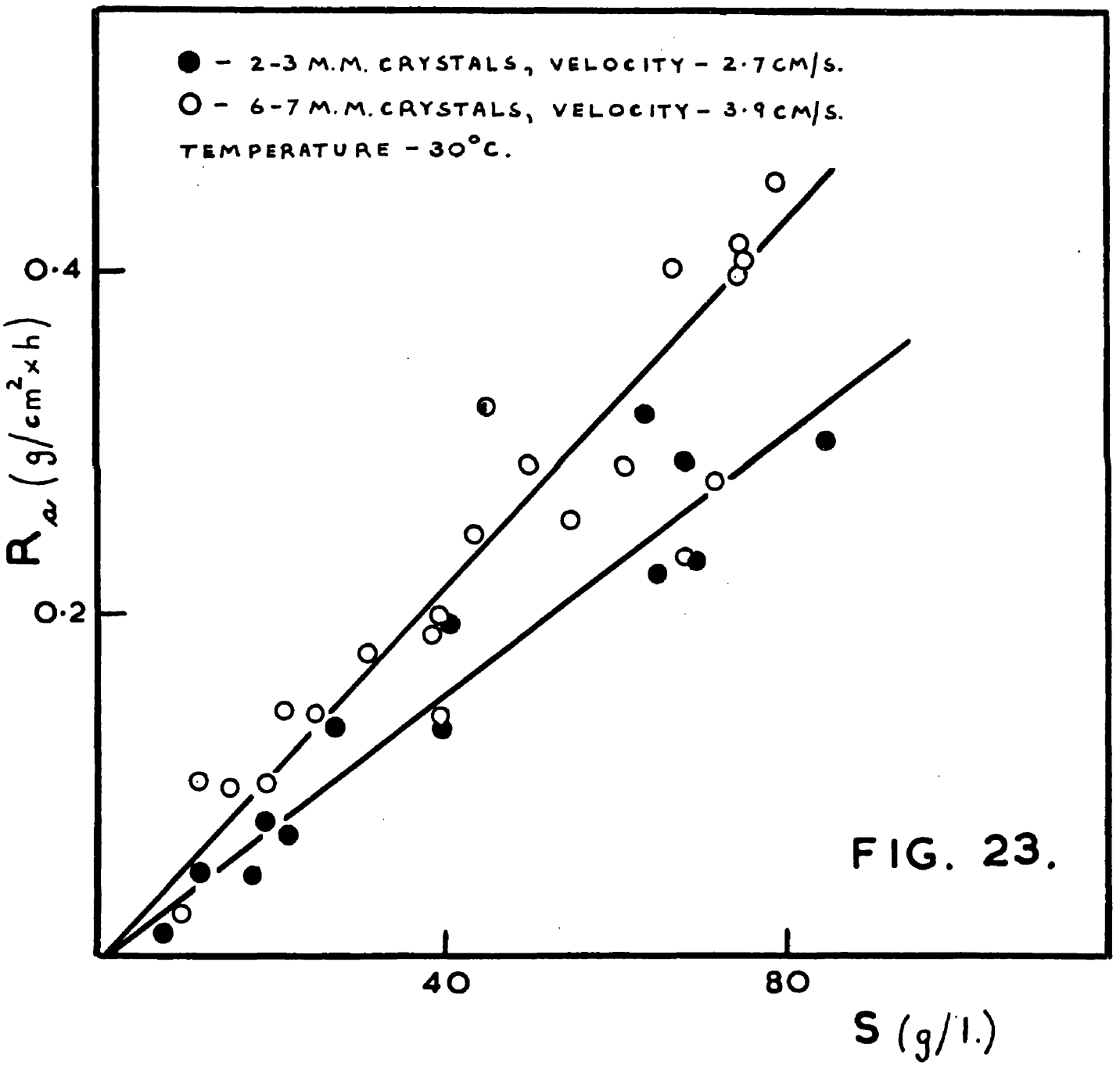

● - 2-3 M.M. CRYSTALS, VELOCITY - 2·7 CM/S.
O - 6-7 M.M. CRYSTALS, VELOCITY - 3·9 CM/S.
TEMPERATURE - 30°C.
0·4
0·2
R_a (g/cm² x h)
40
80
S (g/l.)

FIG. 23.

Two crystal sizes were used, 2-3 m.m. and 6-7 m.m., at flow rates of 2.7 and 3.9 cms./sec. respectively. The effect of forced convection may be considered as varying with the Reynolds Number, or in this case ($V.D._p$). Taking the lines in Fig.23 as guide, the rates of growth are as 1 to 1.4, while the relative values of ($V.D_p$) are 1 to 3.8. This suggests a value for the Reynolds Number index of 0.25 i.e. deposition varies as $R_e^{0.25}$

Effect of viscosity on growth rates.

" Solutions" of Cellofas B were made up containing up to 0.8 gms./litre, and growth rates measured. The additive appeared to have no effect whatever (Fig.24), but it was suspected that it had merely dispersed in a fine suspension. This was conclusively demonstrated by measurements of viscosity (Fig.25), which shows identical values with and without Cellofas B addition. The form of the viscosity-temperature curve with saturated hypo solution is of great interest and will be discussed later.

Comparison of rate of growth and rate of solution.

6-7 m.m. crystals were dissolved in undersaturated solution of known concentration at 30°C, and the rates of solution are compared with rates of growth in Fig.26. The rates of growth fall only slightly below the rates of solution, but they are much more irregular than the latter.

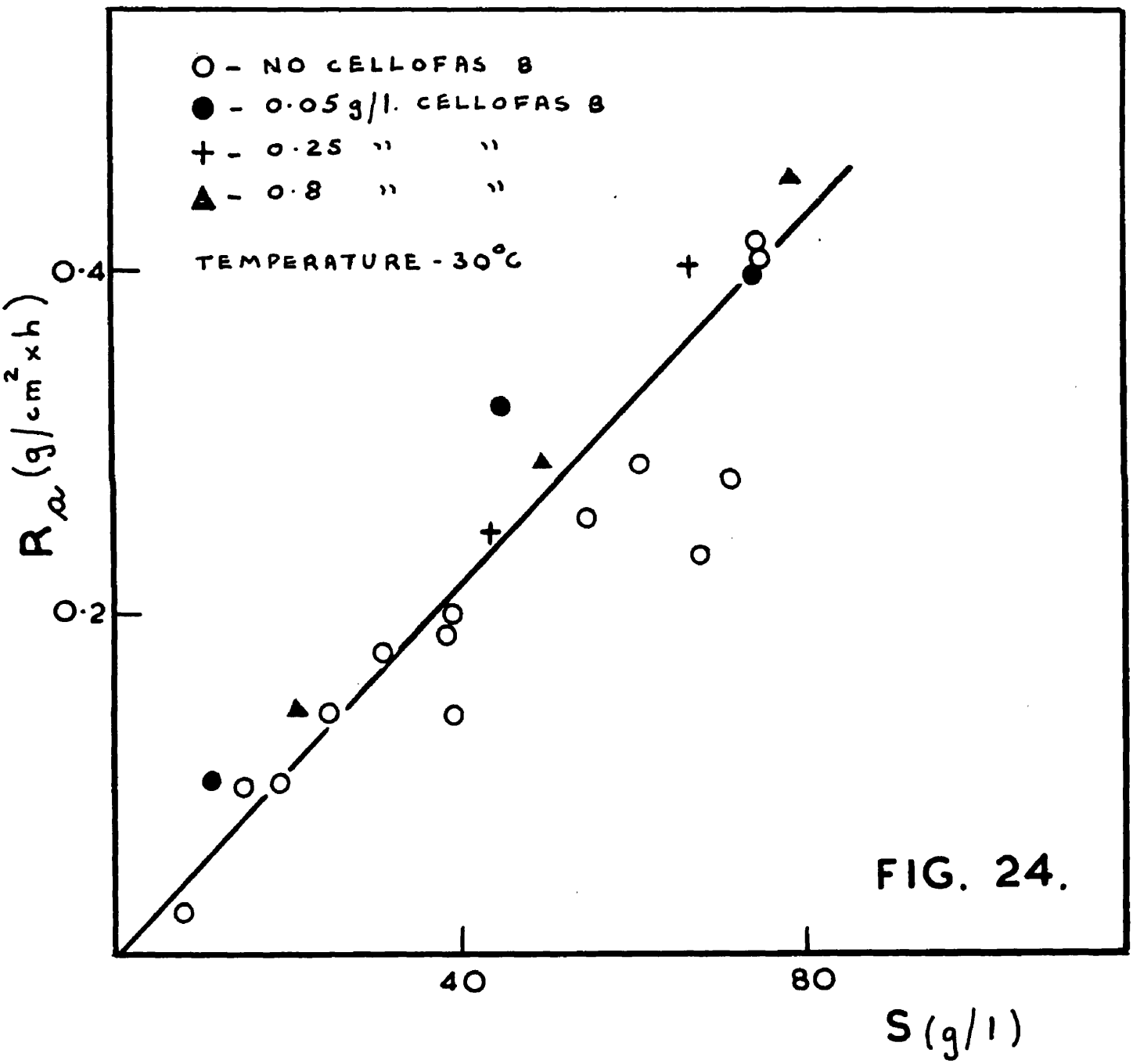

O - NO CELLOFAS B
● - 0·05 g/l. CELLOFAS B
+ - 0·25 " "
▲ - 0·8 " "
TEMPERATURE - 30°C
0·4
0·2
R_α (g/cm² x h)
40
80
S (g/l)

FIG. 24.

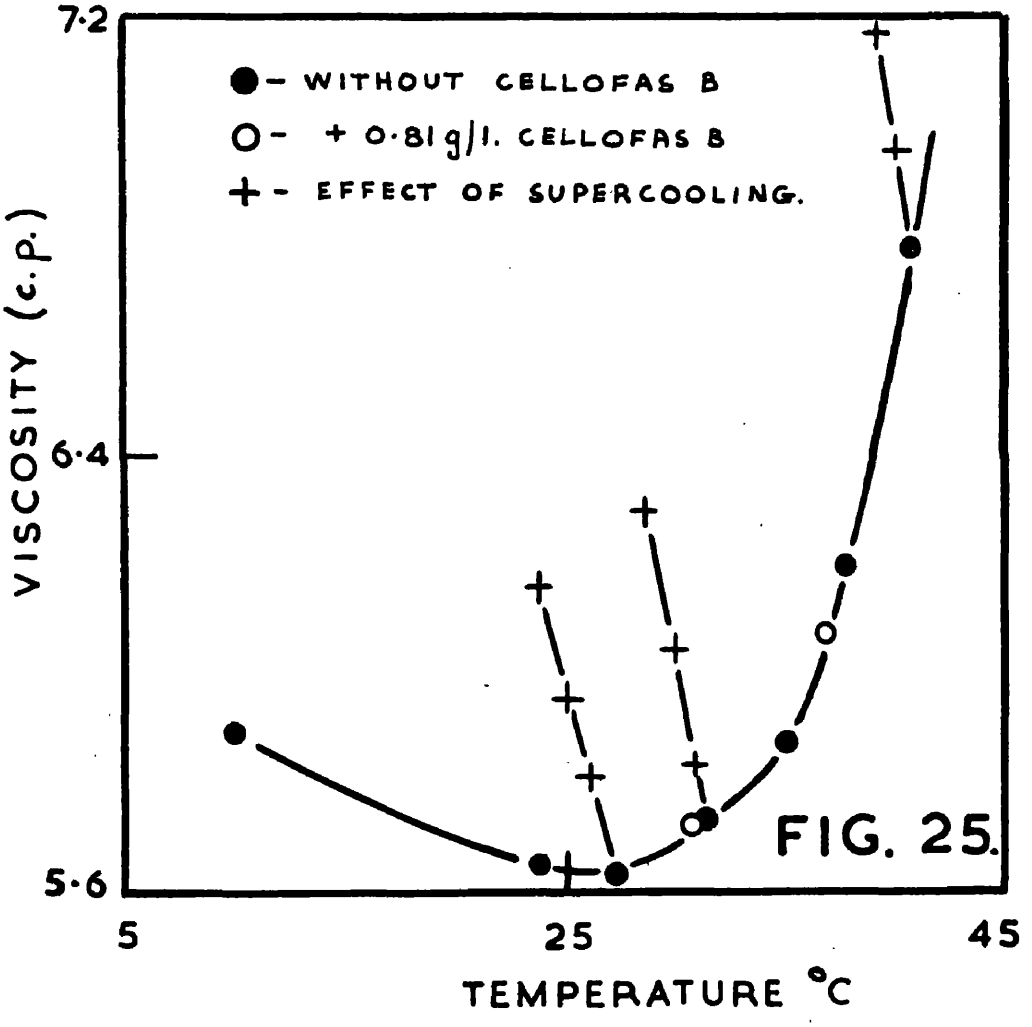

7·2
6·4
5·6
VISCOSITY (c.p.)
● - WITHOUT CELLOFAS B
○ - + 0·81 g/l. CELLOFAS B
+ - EFFECT OF SUPERCOOLING.
5
25
45
TEMPERATURE °C

FIG. 25.

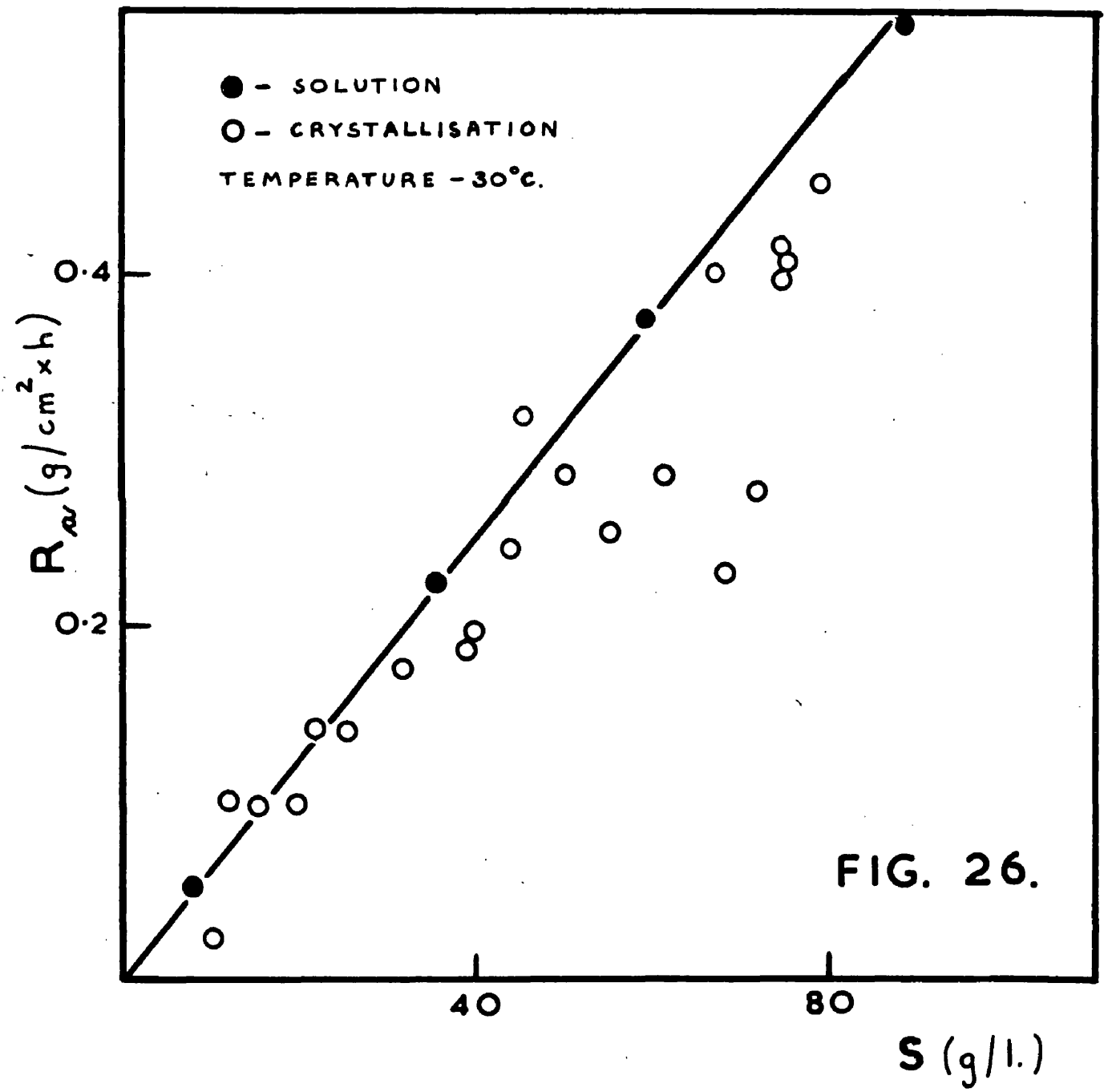

● - SOLUTION
○ - CRYSTALLISATION
TEMPERATURE - 30°C.
0·4
0·2
R_{av} (g/cm² x h)
40
80
S (g/l.)

FIG. 26.

Discussion of results from cooling crystalliser.

The crystallisation rate is found to be proportional to the supersaturation, and temperature has little effect on the crystallisation rate. If the crystallisation process were surface reaction controlled a large temperature coefficient of crystallisation would be expected, as found by Van Hook in the crystallisation of sucrose.[78] On the other hand if the reaction is diffusion controlled there should be a small temperature coefficient of crystallisation as found for sodium chloride in the temperature range (50–73°C). The zero temperature coefficient can be most readily explained by assuming that both processes are active, and that one has a negative temperature coefficient.

The viscosity of the saturated solution, controlled in part by temperature, and in part by solubility, is relatively constant from 20 to 30°C, and moves sharply upwards on either limit. Also the concentration increases greatly above 30°C, and since the diffusivity will probably decrease with increasing concentration, then there should be a tendency for a maximum growth rate at 30°C.

The diffusivity of sodium thiosulphate is given in the I.C.T. as 0.62×10^{-5} cm.^{2}/sec. at 10°C, and a concentration of 1.1 gm. moles/litre. Making the assumption that the diffusivity does not decrease further

with concentration, and that $\frac{D\eta}{T}$ is constant, values for other operating temperatures can be calculated, and hence the effective film thickness if diffusion controls the crystallisation process. The data are set out in Table 6.

Table 6 - Effective film thickness.

Temp. °C	D x 10^5 cm.^{2}/ sec.	K cms./ hr.	Film thickness m.m.
24	0.7	2.0	0.126
30	0.73	4.3	0.06
35	0.73	4.3	0.06
40	0.67	4.3	0.056

The diffusivity is seen to vary very little with temperature, which suggests that the crystallisation process is diffusion controlled. However, the film thickness are about double those considered to show a diffusion controlled process,[74] although there must be some doubt about the diffusivity value used. If the diffusivity does decrease with increasing concentration then the film thicknesses calculated are too large, especially at 35 and 40°C.

There is also the increase in growth rate with Reynold's Number which suggests diffusion control. Cellofas did not dissolve in the saturated solution, and the viscosity could not be increased by this means to

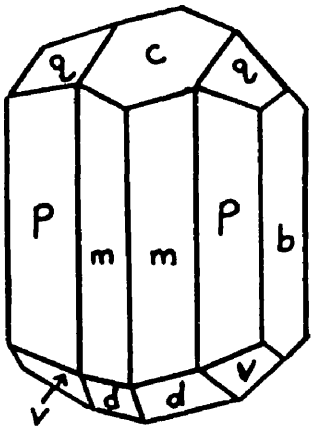
determine more rigorously the effect of viscosity on growth rate.

Fig.26 showed that the rate of solution was only slightly faster than the rate of crystallisation. This would be the case if the diffusion of solute to the crystal surface was followed by a crystal surface alignment which was very fast, but not instantaneous, and of the order of four times as fast as the diffusion mechanism.

The alignment reaction will probably be very sensitive, and may cause the variation found in crystallisation rates. It is possible that at lower temperatures it becomes more important, and may have caused the reduction in crystallisation rates found at 24°C, and that an acceleration in the alignment reaction at 40°C balances the drop in the rate of diffusion.

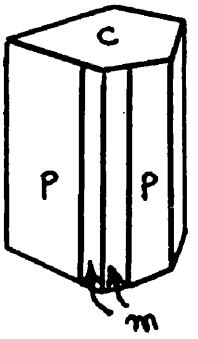
Growth rates were some five times as high as those of Butler.[3] Butler increased the speed of rotation of the crystal until there was no further increase in crystal growth, and assumed that all the resistance to growth then lay in the surface reaction. Holden[38] claimed that the direction of rotation of a crystal has to be reversed frequently to prevent veils and occlusions caused by regions of poor diffusive flow, and that the

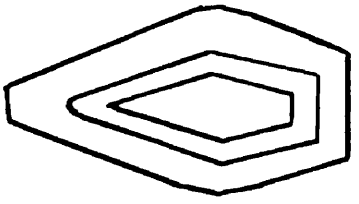
HYPO CRYSTALS



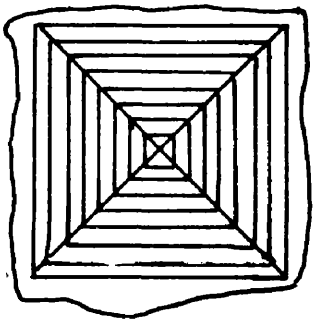
a

b -(010)
c -(001)
m -(110)
P -(120)
q -(011)
d -(111)
v -(131)





c



d

FIG. 27.

rotating crystal can carry round with it an atmosphere of stagnant saturated solution. The present results would seem to prove that the fluidised bed gives more accurate indication of growth phenomena than the method of Butler.

2b. The shape of hypo crystals obtained from fluidised bed crystallisers.

Hypo crystallises as colourless, monoclinic prisms. Fig.27a shows a typical crystal habit. Crystals produced from an evaporative fluidised bed crystalliser were found to have the habit shown in Fig.27b, and the same shape was preserved on further growth in a fluidised bed cooling unit.

Fig.27c is a plan view of the (001) face of the crystal. Of the prism faces {110} was found to be small, and was absent on many of the crystals. In every crystal one of the (010) faces was large, and the other very small. In every case it was found that it was the $(0\bar{1}0)$ face which was small, and the (010) face which was large. Butler found that occasionally one of the (010) faces stopped growing. Once again this suggests that conditions in the fluidised bed were more uniform, and nearer the optimum than the conditions of Butler's experiments.

The crystals were some 1.5 times broader across the (010) and (110) faces than a crystal of commercial

hypo with the same length of prism face. It is known that much of the hypo of commerce is made in a rocking crystalliser.

The prism faces were smooth, lustrous, and optically clear, although occlusions could be seen inside some of the crystals. These occlusions were usually caused by air bubbles sticking to the crystals when they were small. The (001) faces were not smooth, and the crystals were not optically clear through the C axis. On all the faces of $\{001\}$, and the $(0\bar{1}0)$ faces, a deep layer system was visible to the eye, starting from the edges of the crystal and proceeding towards the centre.

At growth rates above 0.22 gms./cm.^{2} x hr. the crystals lost their lustre, and were covered with step like growths. Unlike sodium chloride, hypo crystals at all times preserved their definite faces and edges, even though crystal momentum, and therefore the effects of attrition, must have been of the same order in both systems. This suggests some measure of surface reaction control, with the crystal persistently replacing fractured corners etc.

However, diffusion must play a big part in changing the habit of the crystal. A crystal from the fluidised bed changed its shape when suspended by a thread in the solution, which was saturated at 24°C and

cooled to 18°C. The (010) faces tended to even up in size, and the non prism faces started to grow. Also, crystals grew on the thread supporting the large crystal, and these crystals had the habit of Fig.26a except that {111} was missing; the (010) faces were equally developed, which eliminates the suggestion of impurity causing the difference in their growth rate in the fluidised bed.

Growth formations.

Three types of crystal growth form have been found.

1. Perfect smooth growth on the prism faces of the crystals, except for face $(0\bar{1}0)$.
2. Layer growths on {001} , face $(0\bar{1}0)$, and the underside of crystals grown in stagnant solution.
3. Gross layer growth at high supersaturation.

It has often been stated[5, 64] that good quality crystals can only be grown up to a limiting maximum rate. The present work confirms this, but also suggests that the maximum rate varies from face to face, and that it is only when gross layer formation occurs that the crystal quality really becomes poor.

At low supersaturations the prism faces of the crystal tend to grow smoothly, probably by a screw dislocation mechanism, to give lustrous, optically flat surfaces. When the supersaturation becomes greater than 50 gms./litre the surface becomes covered with rough steps and protruberances which are easily broken

away from the crystal. Crystal growth takes place by deposition of crystalloids, as in the concept of Federov[85,86], or by dendritic growth.

A crystal, lying on the bottom of a pool of unstirred supersaturated solution, showed on its underside the structure shown in Fig.27d. The steps were of the order of 0.01→0.1 m.m. thick, which is many times the molecular height, and the crystal was roughly square in plan. It is suggested that nucleation took place after the Kossel-Stranski[48,49] model at the corners and edges of the crystal, where the supersaturation was high, and that layer completion took place very slowly under the middle of the crystal where the supply of solute was poor. Since growth round the edges of the crystal would take place rapidly, the system results in a "picture frame" slowly moving in towards the centre of the crystal. Fresh nucleation would take place at a corner above this, and an inverted pyramid is produced with the first layer meeting in the centre of the face while the nth layer is starting. Deep layers have often been observed on crystals while the crystals were growing by means of screw dislocations. It has been proposed that piling up of the molecular growth layers is caused by fluctuations in the concentration at the initiating centre. A similar method of layer thickening can be proposed for surface nucleation and layer completion.

The step height of the layers was so great that the real mechanism of growth is doubtful, and could only be ascertained by microscopic examination at very high magnifications. It seems true, however, that growth took place at the corners and edges of the face where the diffusive presentation of solute was highest.

At the operational supersaturation in the continuous crystalliser (12 gms./litre), the crystals showed layer growth on the (001) and ($0\bar{1}0$) faces. In an analogous manner to the above, nucleation takes place at the face corners and edges, and layers spread in towards the centre forming a pit of encirclement. A plan of the (001) face is shown in Fig.26c, and it can be seen how the layer growth follows the shape of the crystal face, i.e. the distance from edge of face to edge of layer remains constant around the crystal. An explanation of this may be that most of the diffusive flow of solute will come from the slower growing prism faces, and the greatest supersaturation and concentration gradient will be at the edges of the face, with reduced supersaturation at the face centre giving reduced growth rate.

For some unknown reason these faces are more easily nucleated than the others, and in particular the $0\bar{1}0$ face is more easily nucleated than the 010 face. Once the $0\bar{1}0$ face grows by surface nucleation it pulls

the diffusion field away from the 010 face which will then grow more slowly.

Crystals which formed on a thread holding a large growing crystal were in a field of low supersaturation because of rising currents of light solution. These crystals had the habit shown in Fig.26a except that {111} was missing. No layers were observed on these crystals, and therefore at low supersaturations, and with no stirring, the whole crystal will grow slowly through screw dislocations. Williams[70] found that lead nitrate grew at high supersaturations by surface nucleation, and at low supersaturation by screw dislocations.

The faces which grew by surface nucleation were rougher in appearance than the prism faces, and the crystal was not clear through the C axis. The product crystals, though clear enough for an industrial crystal, and of better quality than the pea crystals used to prepare solution, did not have the perfect lustre and clarity of the small crystals growing on the thread, or of the crystals shown in Butler's work. This would of course be caused by slight misfit in the layers.

It has often been claimed that slight faults in the crystal will increase the speed of growth by a factor of about four. The growth rate found in this work was five times that found by Butler. The increased

growth rate, and the imperfection in optical quality, are obviously caused by the layer formations on the fast growing faces. Butler used the same range of supersaturation, and yet he only found rapid growth of the $0\bar{1}0$ face occasionally. Thin diffusion films are produced by the turbulence of the fluidised bed, and these must aid surface nucleation at moderate supersaturations (12 gms./litre), which are greatly below the 50% excess of saturation concentration demanded by theory. There is, in a fluidised bed, considerable rubbing of solid surface, which may cut down the thickness of any stationary layer and increase surface faults; some attempts have been made to explain heat transfer rates by this hypothesis.

2c. Continuous production of Hypo crystals.

Crystals of Hypo were grown continuously in the laboratory Oslo crystalliser which has been previously described. Crystallisation was carried out by evaporation under vacuum at 30°C, so that a comparison could be made with sodium chloride production under similar conditions. Cold saturated solution was fed to the plant.

It was found possible to produce pea crystals (6 m.m.) from 800 gms. of bed at a production rate of 200 gms./hr. The fluidisation velocity was 1.6 cms./sec., and the bed was 1.7 ft. deep. Product crystals are

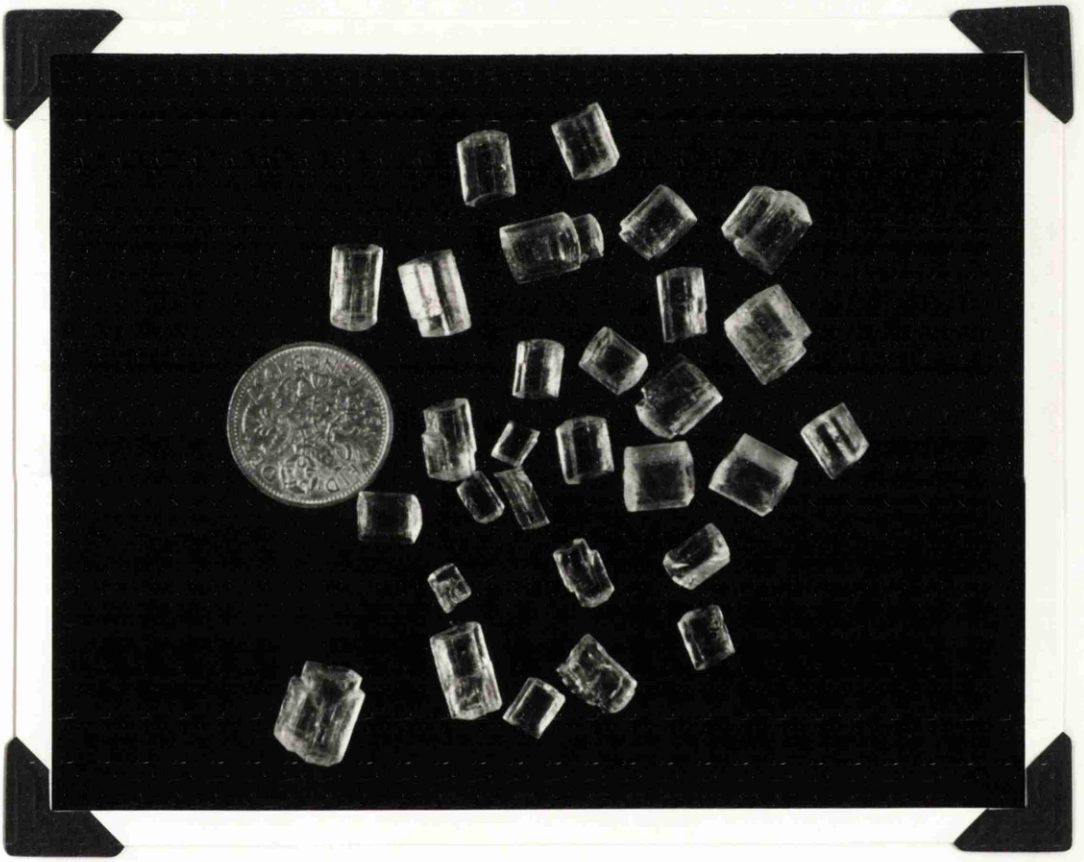


Figure 28. Product hypo crystals.

shown in Fig.28.

The crystal shape has been previously discussed, and the crystals were clear, with a good lustre, and there was very little twinning. The bed consisted of large 6 m.m. crystals with a very few small crystals above it. The deposition concentration was calculated from the production rate and the solution flow to be 2 gms./litre, and the rate of growth was 0.05 gms./cm.^{2} x hr.. From the cooling results the actual supersaturation was 12 gms./litre, and therefore the inlet supersaturation to the bed was 13 gms./litre, and the exit supersaturation was 11 gms./litre.

The production rate of 200 gms./hr. is equivalent to 40.5 lbs/hr. x ft.^{2} of crystalliser cross-sectional area, for 6 m.m. crystals, at a bed height of 1.7 ft.

In starting the unit, 2.5 litres of solution were saturated in the plant at 40°C and cooled over 30 minutes to 36.5°C. 300 gms. of product were obtained of 1.5 m.m. size, after spontaneous nucleation had occurred. If a clear solution is evaporated to the nucleation point the nuclei formed are relatively few in number, and grow rapidly. By removing half of the crystals periodically a bed of large crystals is soon developed. There is no such difficulty as that met with in starting a sodium chloride unit.

Metastable limit.

Hypo is able to hold a large metastable limit before spontaneous nucleation occurs. The degree of supersaturation possible without nucleation depends very much on the conditions under which the solution is placed. It is possible to cool a hot, concentrated, hypo solution to room temperature without crystallisation taking place.

When circulating in the plant solution was supercooled by 2.4°C at 30°C before nucleation took place. This gives a metastable limit of 90 gms./litre. However, a solution which was stirred rapidly in a beaker nucleated at 50 gms./litre supersaturation at 30°C. The mechanical impact in rapid stirring must be greater than the impact taking place in passage through a Monopump. There is also the important factor to consider that growth becomes of a poor type at 50 gms./litre, and therefore we may say that the metastable limit at 30°C is, for practical purposes, 50 gms./litre, or a supersaturation ratio of 1.048.

Design of a large unit.

Assuming an inlet concentration of 40 gms./litre, and an exit concentration of 10 gms./litre, then the log. mean supersaturation is 22 gms./litre. The supersaturation system, whether by cooling or evaporation,

must increase the supersaturation by 30 gms./litre on each passage through the system.

At a supersaturation of 22 gms./litre the rate of growth is 0.095 gms./cm.^{2} x hr; and at a solution velocity of 1.6 cms./sec., the production rate will be 360 lbs./hr. x ft.^{2} of cross-sectional area. If the bed consists of 6 m.m. crystals then there must be 500 lbs. of crystals per sq. ft. of crystalliser cross-sectional area, to absorb the supersaturation. From the suspension density of the small crystalliser this would give a bed 11 ft. deep.

A crystalliser 4 ft. in diameter and 12 ft. deep will give a production rate of 1.8 tons per hour of large hypo crystals. It was not possible in the time available to check these conclusions with the 12 ins. diameter crystalliser.

2d. Conclusions.

The rate of growth of hypo has been determined in a fluidised bed over a temperature range of 24→40°C The crystallisation is first order with respect to supersaturation, and temperature has little effect on the crystallisation rate over the temperature range studied.

The mass transfer coefficient in 4.3 gms./cm.^{2} x hr. x gm./c.c..

The results suggest that crystallisation takes place by diffusion to the surface followed by a very fast, but not instantaneous orientation at the crystal surface. Solution is only slightly faster than crystallisation at the temperature and solution velocity used in the experiments.

The crystal shape produced seems to be particular to fluidised bed crystallisers, and is simpler than that of crystals grown from stagnant solution or rocking crystallisers.

The metastable limit for nucleation is of the order of 90 gms./litre but at supersaturations of above 50 gms./litre the crystal quality becomes poor. The nuclei produced after spontaneous nucleation are few in number and grow rapidly, and therefore a bed of crystals can be readily formed from a saturated solution free of crystals.

The mass transfer coefficient is only one tenth of that found for sodium chloride, but because of the high metastable limit possible production figures are high. 6 m.m. crystals were obtained from a fluidised bed 1.7 ft. deep at a rate equivalent to 40 lbs./hr. x ft.^{2} of crystalliser cross-sectional area. It is estimated that 1.8 tons/hr. of 'pea' crystals could be obtained from a crystalliser with a suspension holder 4 ft. in diameter and a crystal bed 11 ft. deep.

3. The Crystallisation of Barium Hydroxide Octahydrate (Barium Hydrate).

Barium hydroxide solutions are strongly alkaline, and alkaline earths are normally difficult to crystallise. When cooled rapidly a hot solution of barium hydroxide crystallises dendritically to give very thin, fragile plates. Barium hydroxide octahydrate crystals rapidly absorb carbon dioxide from the air, and the crystals become covered with a layer of barium carbonate. This covering is not protective, and therefore the ideal shape of crystal to resist attack is a sphere. Moreover, a spherical type of crystal filters much faster than a flake.

Sodium chloride has a fairly low solubility, and a small temperature coefficient of solubility; hypo has a high solubility and a large temperature coefficient of solubility; barium hydrate has a fairly low solubility and a large temperature coefficient of solubility. The physical properties of barium hydrate showed it to be quite a suitable solute for extending the range of experiment. Solubility data were taken from the I.C.T. (1st Edn. Vol.4, p.236).

3a. Rate of crystal growth.

Crystals used in the experiments were 12-18 mesh, and were prepared in the laboratory continuous crystalliser.

Solutions were prepared from an industrial grade of barium hydrate supplied by Laporte Chemicals Ltd., and the solution was filtered before use to remove any barium carbonate present. The crystals were not as regular in shape as the sodium chloride or hypo crystals, and the specific surface area was estimated by weighing a batch of crystals, and measuring the dimensions of the individual crystals by micrometer.

The fluidising velocity was 3 cms./sec. through the empty fluidisation tube, and the duration of each run was 10 minutes. Crystallisation was carried out at 23, 33 and 40°C. The weight of crystals in the bed at the start of a run was 4 gms.

The effect of supercooling on rate of growth is shown in Fig.29. The rate of growth is expressed as gms. of barium hydroxide octahydrate crystallised per hour per gm. of crystal in the bed at the start of the run, and the supercooling is given in degrees Centigrade. These results have been recalculated in Fig.30 to show the rate of growth as gms./cm.^{2} x hr, and the supersaturation as gms./litre.

When the growth rate increased beyond 0.05 gms./cm.^{2} x hr., i.e. a supersaturation of 2.8 gms./litre, the crystal quality became poor, and at high supersaturations (4 gms./litre) the surface became covered with tiny, soft flakes. Whenever these flakes

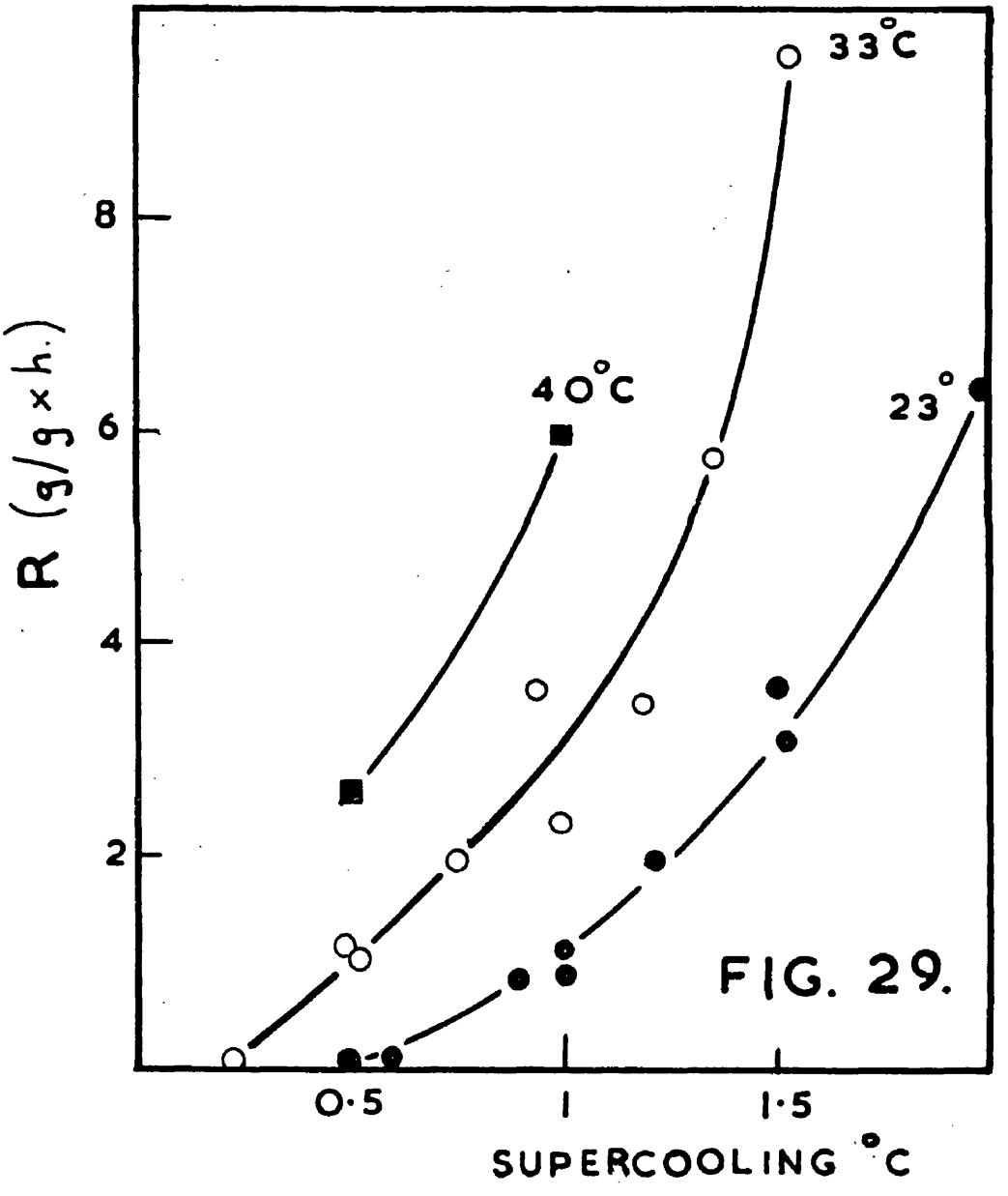


FIG. 29.

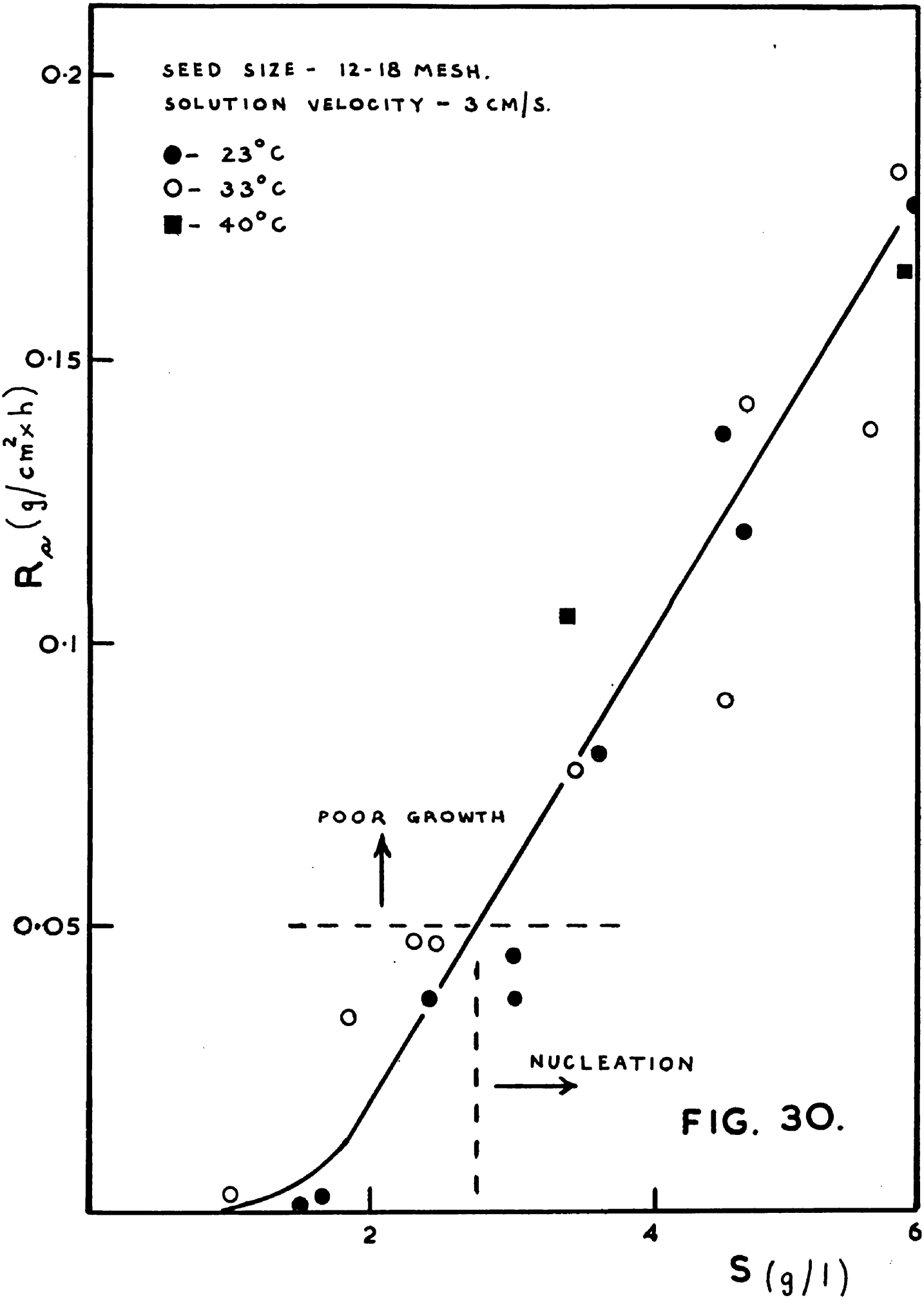

SEED SIZE - 12-18 MESH.
SOLUTION VELOCITY - 3 CM/S.
● - 23°C
○ - 33°C
■ - 40°C
0·2
0·15
0·1
0·05
R_ω (g/cm²×h)
POOR GROWTH
NUCLEATION
2
4
6
S (g/l)

FIG. 30.

formed they tended to fragment and form new crystals, but in the batch plant any fragments were swept away with the fluidising liquid flow into the waste receiver.

As in the case of hypo, there is no change in growth rate with temperature, and the rate is proportional to the supersaturation. However, the crystals show a resistance to growth up to a limit of 1.0 gms./litre, which is twice the value found for sodium chloride at low temperatures. To ensure saturation, the solution was stirred for 24 hours at constant temperature before passage through the plant, but the growth rate was negligible below 1 gm./litre supersaturation.

The resistance to growth may not be on the barium hydrate crystal surface, but on the barium carbonate layer present on the crystal. That is, the metastable limit for barium hydroxide crystallisation on a barium carbonate substrate is 1 gm./litre. There was no time available to attempt growth measurements, under batch conditions, on crystals which had never been in contact with carbon dioxide. The nature of this minimum supersaturation for growth is very important since the possible output will depend on this factor. In effect the minimum supersaturation for growth is a "blank" value which reduces the possible driving force for

growth. In an industrial plant carbon dioxide must be excluded.

The diffusivity of barium hydroxide is given in the I.C.T. as 1.5×10^{-5} cm.^{2} / sec. Assuming that the restriction to growth below 1 gm./litre is caused by the carbonate film, then the mass transfer coefficient is 47.4 gms./cm.^{2} x hr. x gm./c.c., which is of the same order as the mass transfer coefficient for sodium chloride. The film thickness through which diffusion takes place is 0.012 m.m., if a diffusion controlled mechanism is assumed. Such a thickness is quite normal and closely comparable with those already suggested for sodium chloride crystallisation. In view of the negligible temperature coefficient, diffusion control seems almost certain.

Effect of dextrin on crystal growth.

In the continuous production of barium hydrate it was found that dextrin had an effect on the crystal structure, and therefore the effect of dextrin on the crystal rate was studied. The rates of crystal growth from pure solution at 33°C are compared in Fig.31 with the rates of crystal growth from a solution containing 1 gm./litre of dextrin. Over the range of supersaturation studied the dextrin addition reduced the growth rate considerably. As the crystals were " preformed" the

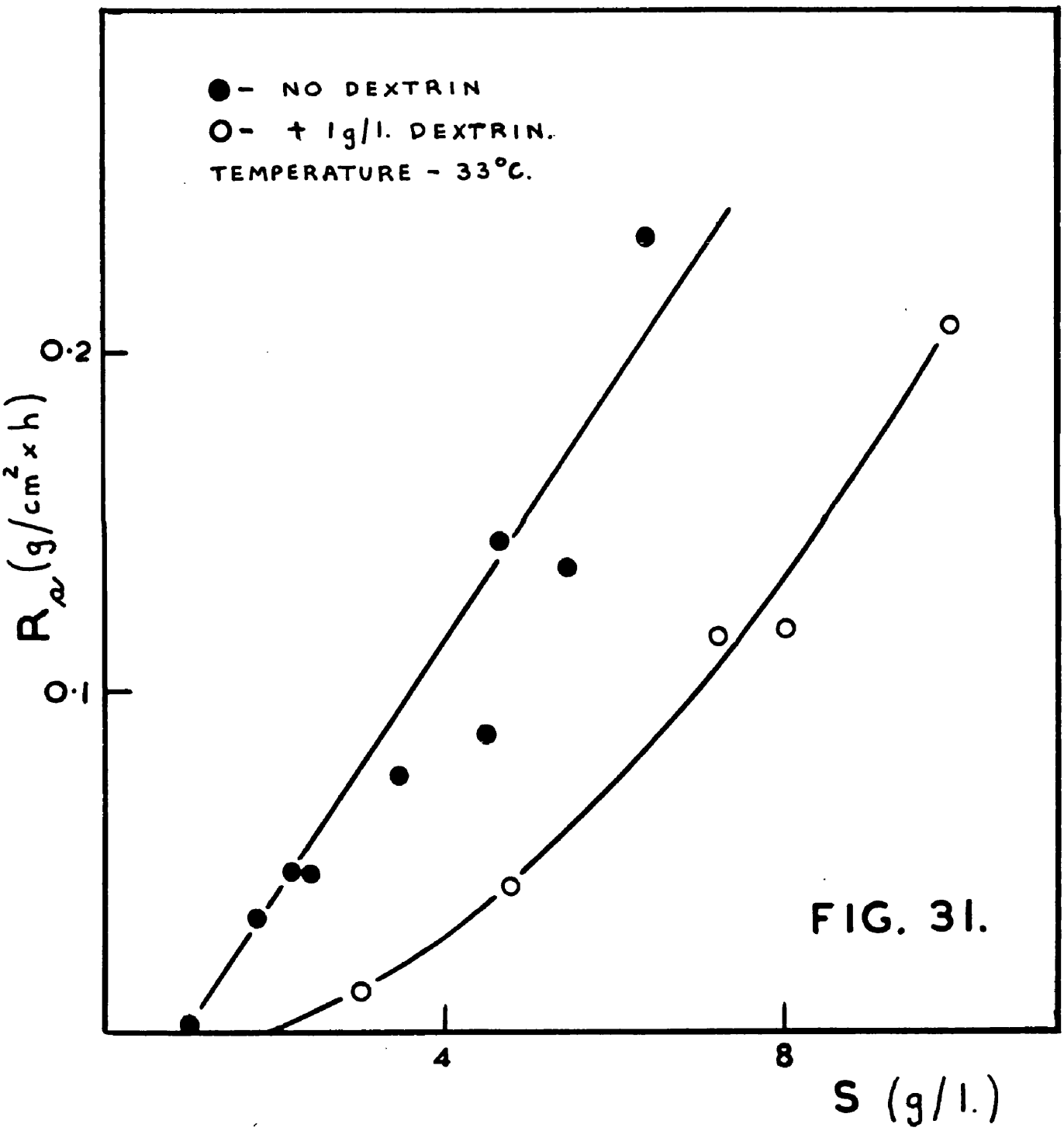

● - NO DEXTRIN
○ - + 1 g/l. DEXTRIN.
TEMPERATURE - 33°C.
0·2
0·1
R_∞ (g/cm² x h)
4
8
S (g/l.)

FIG. 31.

effect of dextrin on crystal shape could not be determined here. In continuous runs it was observed that "flake" growth was checked. Clearly the dextrin had slowed down surface adjustment, andrates might no longer be diffusion controlled.

3b. Crystallisation in the laboratory continuous crystalliser.

The glass plant was reconstructed as shown in Fig.32 to bring about crystallisation by cooling. Hot solution was saturated in a temperature controlled bath, and transferred to vessel E where it was kept hot by water at 65°C circulating through the jacket. The hot saturated solution was added to the plant through a valve, and the rate of dropping adjusted to give approximately the correct feed-rate. The solution in the plant was cooled by tap water in cooler D to 22°C and the cold waste solution was run out at F. Product was removed from the base of the crystalliser at half hourly intervals.

The plant was operated at a circulating solution temperature of 22-23°C (solution concentration 77 gms./litre), and a feed solution temperature of 45°C (solution concentration 184 gms./litre). The operational conditions and product sizes are shown in Table 7.

COOLING CONTINUOUS CRYSTALLISER

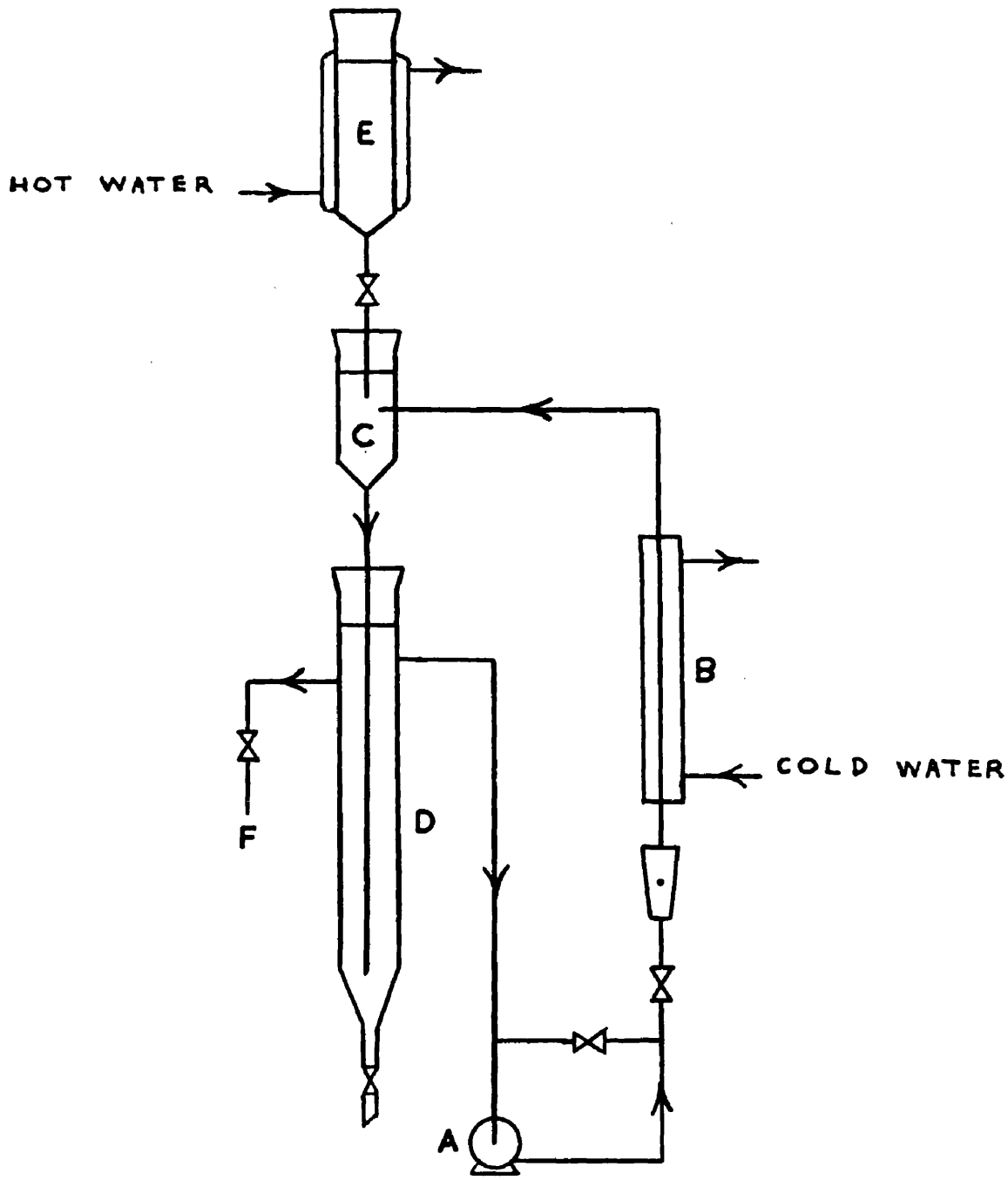


FIG. 32.

Table 7 - Size of Product Barium Hydrate Crystals.

Prodn.rate (gms./hr.)	Wt. of cryst. bed(gms.)	Duration of run (hrs.)	+10 mesh	10-12	12-18	-18
50	400	24.5	20	10	50	20
50	800	16.5	15.5	15.5	57	12
100	800	16.0	23	25	47	5

Barium hydrate can therefore be crystallised to give an 80% + 18 mesh product in a fluidised bed crystalliser.

The product crystals were of good quality (Fig.33) and the crystals were just as hard as sodium chloride crystals. Most of the crystals were ovoids, discs, or spheres, with no edges or corners visible, but when they were cut open they showed good lustrous surfaces. A crystal was occasionally obtained which had a bipyramidal habit, and the ovoids, discs, and spheres could have been formed easily from this habit. The crystals were in general much more rounded than the sodium chloride crystals, and this agrees with the very low value of film thickness found, i.e. that crystal growth is almost completely diffusion controlled.

Crystals formed by spontaneous nucleation in the absence of a seed bed were very flaky and thin, and developed into thin flakes with a low strength. They had grown in a dendritic fashion, and it took a considerable time for these flakes to be removed from

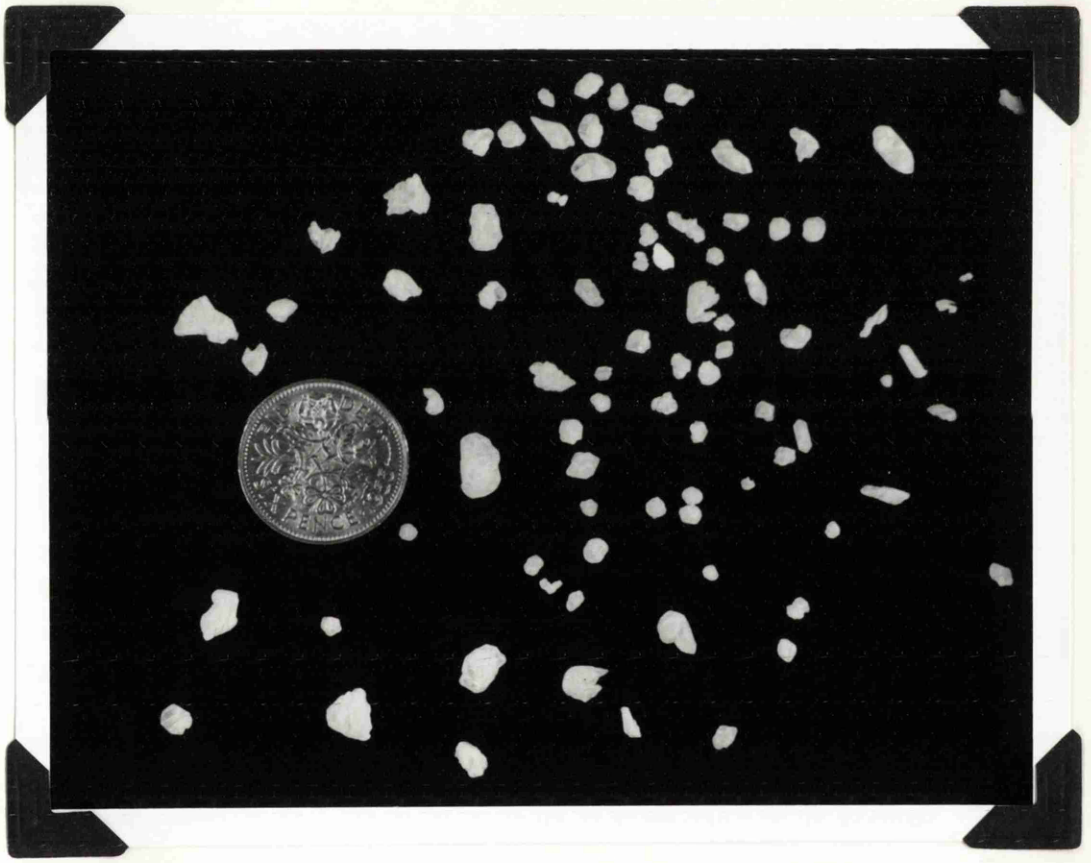


Figure 33. Product barium hydrate crystals.

the bed as product, and be replaced by more solid, bulky crystals. It was found that the addition of 1 gm./litre of dextrin aided the development of the flaky crystals into harder, spherical crystals. As has been shown, dextrin reduces the rate of crystal growth.

Cooling produced crystal growth in the feed tube when solution saturated at 60°C was added to the plant. This would be easier to avoid in a large plant by means of steam tracing, but at this high concentration (376 gms./litre) there will always be a danger of nucleation and subsequent blockage in the feed pipe; and also local concentration fluctuation at the point of addition will be higher, with subsequent greater nucleation.

The surface area of the bed was 14,000 $cm.^2$ and at a production rate of 100 gms./hr. the growth rate was 0.0072 $gms./cm.^2 \times hr.$ This is a growth rate which will give good quality growth (Fig.30).

The small plant was only run up to a production rate of 100 gms./hr., because it was thought it would be easier to control low feed rates of hot saturated solution on the semi-technical plant than on the small plant. There were no problems of nucleation or crystal growth in the cooler at this rate, with the plant working at 22-23°C, and the cooling water inlet temperature at 16.5°C.

3c. Barium hydrate production in the semi-technical plant.

The pilot plant was altered as shown in Fig.34 to convert it to a cooling crystalliser. Hot saturated solution was pumped from the saturation tank F up through an electrically heated pipe line to the mixing vessel E. It was then mixed with the circulating solution, which was cooled in heat exchanger D. The feed and circulating flows were now measured by rotameters C. A fines separator G was placed in the circulating stream.

At first it was attempted to grow a bed of crystals from cold saturated solution by adding hot saturated solution at 45°C. Masses of woolly flocs were formed, which on filtration proved to be composed of tiny flakes. These flocs were still formed after the addition of a bed of 50 lbs of large crystals. It was discovered that the flocculation was caused by air which entered in the vortex in the mixing vessel, and travelled with the solution flow. This was prevented by bypassing the mixing vessel, and merely using it as a liquid seal. The feed solution was then injected straight into the solution flow. It may be noted that it is not possible to inject hot saturated solution through a pipe projecting below the circulating solution level. The projection soon blocks up.

After the problem of flocculation was solved it

COOLING SEMI-TECHNICAL PLANT

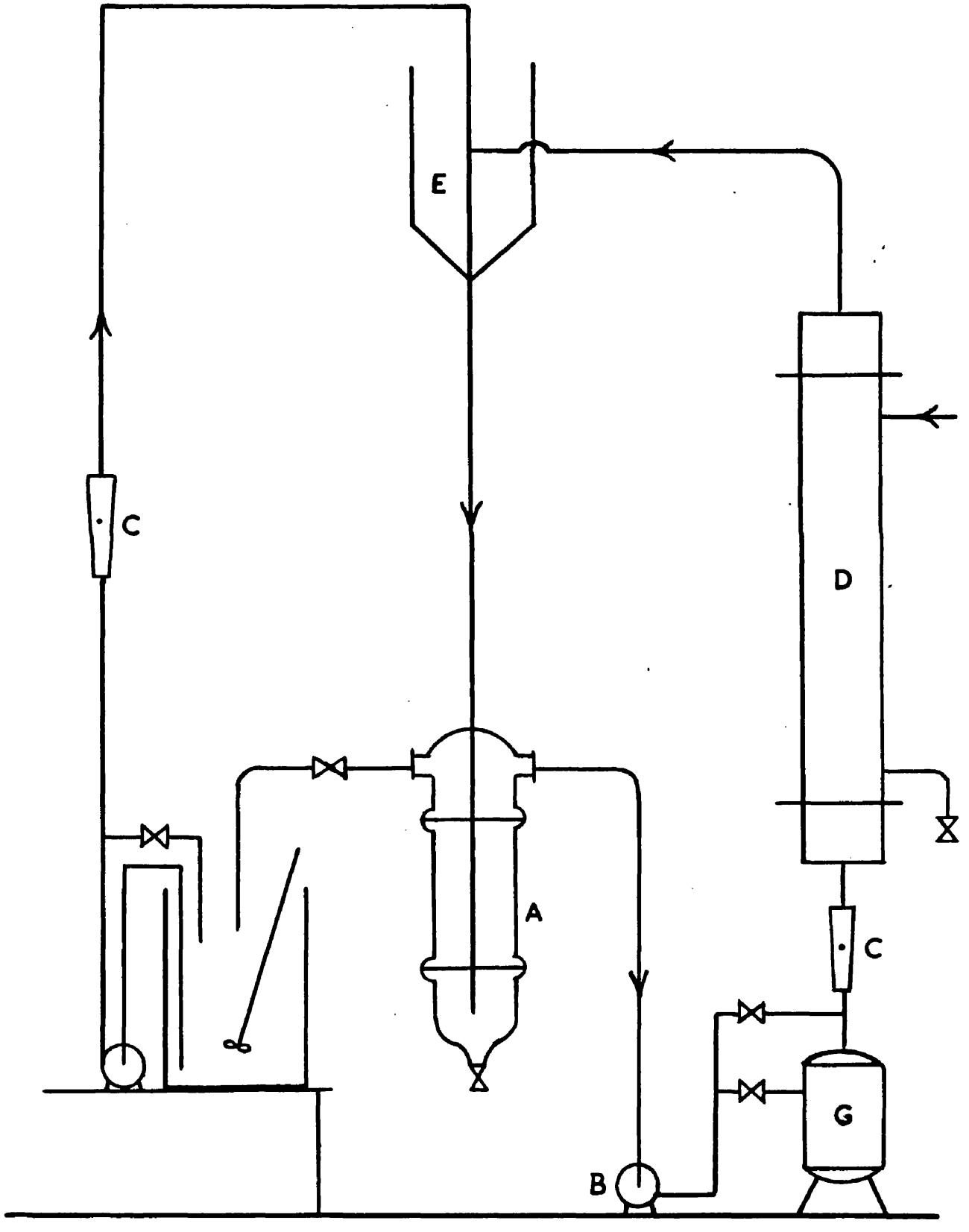


FIG. 34.

was found that the nucleation rate was too high. At a production rate of 10 lbs./hr. some 9 lbs. of fines were being produced for every 1 lb. growth on a bed of 60 lbs. of crystals. Also the solution flow dropped from 35 galls./min. to 25 galls./min. over 6 hours, and obviously crystal growth was taking place in the cooler. The growth in the cooler could be removed by steaming the outside of the tubes.

The temperature of the circulating solution flow was 26°C and inlet cooling water temperature was 16.5°C. The temperature difference of 9.5°C across the heat exchanger tubes seemed rather high. In order to decrease the temperature difference the cold water flow through the heat exchanger was increased from 4 to 27 galls./min., and the water flow was made counter-current instead of co-current. This proceedure successfully lowered the plant temperature to 21°C at the start of a run i.e. a temperature difference of 4.5°C, even lower than that used in the laboratory Oslo crystalliser. However, the temperature of the circulating solution rose steadily to 25°C, fines were still produced, and crystals grew in the heat exchanger tubes and reduced the flow. It was not therefore a question of poor heat transfer causing crystal growth because of a high temperature difference, but rather the formation of crystals in the tubes, even at the low temperature difference of 4.5°C, causing

poor heat transfer.

To investigate the possibility of stainless steel catalysing the nucleation of barium hydroxide the glass tube cooler in the small plant was replaced with a stainless steel cooler of about the same dimensions. The same conditions were reproduced as in the glass cooler operation, and there was no growth in the cooler, or fines formation, and therefore there was no catalytic effect.

The stainless steel tubes in the big plant had, of course, been used for sodium chloride production, and it is known[87] that pitting is produced in stainless steel by boiling brine, especially in the presence of solid crystals. To reproduce this effect the stainless steel tube which had been used in the small plant was etched with hydrochloric acid, and a temperature difference of 5.5°C set up across the tube in the small plant. Nucleation was produced, though not as excessive as in the pilot plant, and crystal growth was observed in the tube where the cooling water entered the heat exchanger. This annular deposit grew until it blocked the tube.

Since the fluid flow on both sides of the heat exchanger was of the same order, then the equilibrium temperature of the tubes would be 19.2°C. If crevices are present in the tube wall on the solution side, then

the solution will tend to remain in these crevices, and become supercooled by 2.8°C (i.e. over the metastable limit) even though the general solution flow is turbulent. Now this degree of supercooling will cause nucleation and crystal deposition on the tube walls.

There was no time available to replace or retube the heat exchanger, and therefore the temporary expedient was tried of passivating the tubes with concentrated nitric acid, and coating with a thin layer of bakelite resin. Passivation did not prevent either the nucleation or the growth in the cooler, but the layer of resin successfully prevented nucleation. There was, however, some crystal growth in the cooler.

A full scale plant would require two heat exchangers in parallel, so that one could operate while the other was being steamed. If the tubes were of stainless steel, as high a polish as possible should be given to them. There is also a possibility of using other heat transfer materials. Impervious graphite probably has a surface which would prevent crystal growth and nucleation, and moreover the high thermal conductivity would help to reduce the size of a heat exchanger. This would have to be large to carry a large heat load at a temperature difference of only 5°C.

3d. Conclusions.

(1) The rate of growth of barium hydrate is linear with respect to supersaturation, and there is a zero temperature coefficient of crystallisation over the temperature range 20-40°C. The crystallisation is probably under diffusion control, and the mass transfer coefficient is 47 gms./cm.^{2} x hr. x gm./c.c.
A minimum supersaturation for growth was found, of value 1 gm./litre, but it was not proved whether this is a true barrier, or whether this is the concentration required to build upon a barium carbonate layer.

The crystal growth becomes of a poor, flaky type above 0.05 gms./cm.^{2} x hr., and the metastable limit of nucleation is of the order of 2.8 gms./litre.

(2) It was possible to produce barium hydrate continuously in the laboratory plant. The crystals were good quality, clear and with a good lustre before being attached by carbon dioxide. 80% of the product was above 18 mesh, but the crystal shape was very irregular, and of a spherical type. The crystal production rate was equivalent to 10 lbs./hr. x ft.^{2} of crystalliser cross sectional area.

Pitting in the heat exchanger tubes of the semi-technical plant caused excessive nucleation, and growth in the tubes. The temperature difference across

the tubes should be kept below 6°C, and the tube surface on the solution side should have as high a polish as possible. With a good smooth surface on the tubes a production rate of 40 lbs./ft.^{2} x hr. should be possible before nucleation becomes excessive, both from the bulk of the solution and on the crystal surface.

D. General Discussion.

(a) The effect of diffusion on the rate of crystal growth.

It was found that normally the diffusive presentation of solute to the crystal surface was rate controlling, and the rate of surface reaction was subsidiary. Increase of temperature produced a greater dependence on the rate of diffusion.

In recent years many workers have investigated the rate of growth of single crystals, both by rotation of the crystal, or by pumping solution past a stationary crystal. In every case they found a reaction which was governed by the rate of diffusion at low relative velocities of crystal and solution, but above a certain critical velocity diffusion was no longer important, and crystallisation was surface reaction controlled. This minimum velocity varied with the solute, but was of the order of 1 ft./sec. [3,35,37,38]

Now the velocity of solution past the crystal in this work was of the order of 0.2 ft./sec., and this velocity remained approximately constant with fluidising flow, since a fluidised bed is free to expand. The fluidising velocity to lift the crystal will vary with crystal size, and crystal and solution density, but most inorganic crystals have a density of from 1.5 - 2.5 gms./c.c.

and a solution density of circa 1.2 gms./c.c., and therefore the relative velocity of crystal and solution will be about 0.2 ft./sec., for the crystal size range studied. Therefore it is possible that in all crystallisation in fluidised beds the diffusion step will be extremely important, as was found for the three solutes experimentally tested. It may be noted that in all industrial crystallisation, whether by mechanical agitation or natural boiling, the crystal-solution relative velocity will be well below 1 ft./sec.

As added evidence it may be stated that hypo, under continuous production conditions, was found to grow almost as fast as it dissolved, although hypo, with its beautifully formed faces, might be considered to be a surface reaction controlled crystal.

One unexplained point is that Butler[3] after increasing the rate of rotation of a hypo crystal until further increase made no difference to the growth rate (i.e. diffusional resistances were negligible), only found a growth rate of one fifth that found for crystals growing in a fluidised bed where diffusional resistances were quite high. The only explanation seems to be that the quality of Butlers single crystals was superior, and the faults and imperfections in the Oslo crystals increased their growth rate greatly, so that the rate of solute presentation by diffusion became

extremely important. The continuous collisions may have caused these faults, which were portrayed by the thick layers on certain crystal faces.

It should be noted that industrial crystals need not have the perfect regularity of single crystals which are required for optical and electrical purposes. If the slight misfits in the layers only decrease the crystal quality slightly, but also increase the growth rate, then they are beneficial from an industrial point of view in reducing the size of apparatus necessary for a given production weight.

Sodium chloride and barium hydrate crystals tended towards a spherical habit. Now this rounding was probably caused by attrition, especially since the larger crystals were more rounded than the small, but since corners and edges did not grow again it is suggested that the surface reaction rate was rapid compared with rates of diffusion, as was proved by measurements of growth rates, and that the surface reaction is anisotropic. The relative sharpness of the corners and edges of crystals grown in fluidised beds will, to some extent, indicate the importance of the surface reaction in the crystallisation mechanism.

It was found for each solute tested that increase of supersaturation beyond a certain limiting value produced a very poor type of crystal growth, e.g. irregular

granules and stepped growths covering the surface. This was a form of dendritic growth, and occurred just below the supersaturation where new crystals appeared in the solution. It is possible that these new crystals were formed from particles rubbed off the crystal surface and that true nucleation of the bulk solution never occurred. The supersaturation value causing dendritic growth and nucleation will be a function of the solute diffusivity, but the solution viscosity and ease of packing of the solute molecule will also affect the value. Sodium chloride, barium hydrate, and hypo, have metastable limits for nucleation at 30°C of 1.6, 2.8, and 50 gms./litre respectively (supersaturation ratios of 1.005, 1.025 and 1.048) and the values are roughly in the order of decreasing solute diffusivity (1.8, 2.0, and 0.7 x 10^{-5} $cm.^2/sec.$) and increasing molecular weight (58.5, 315, and 248 gms./mole).

Since it has been shown here that diffusion plays the major role in the crystallisation of the three solutes examined, it is interesting to compare the experimental results with those of other workers, and to try to achieve an overall correlation for the effect of diffusion on growth rate. This is shown in Fig.35, which is a plot of Mass Transfer Coefficients against Schmidt Numbers. Only a limited number of suitable data is available, and results at low temperatures

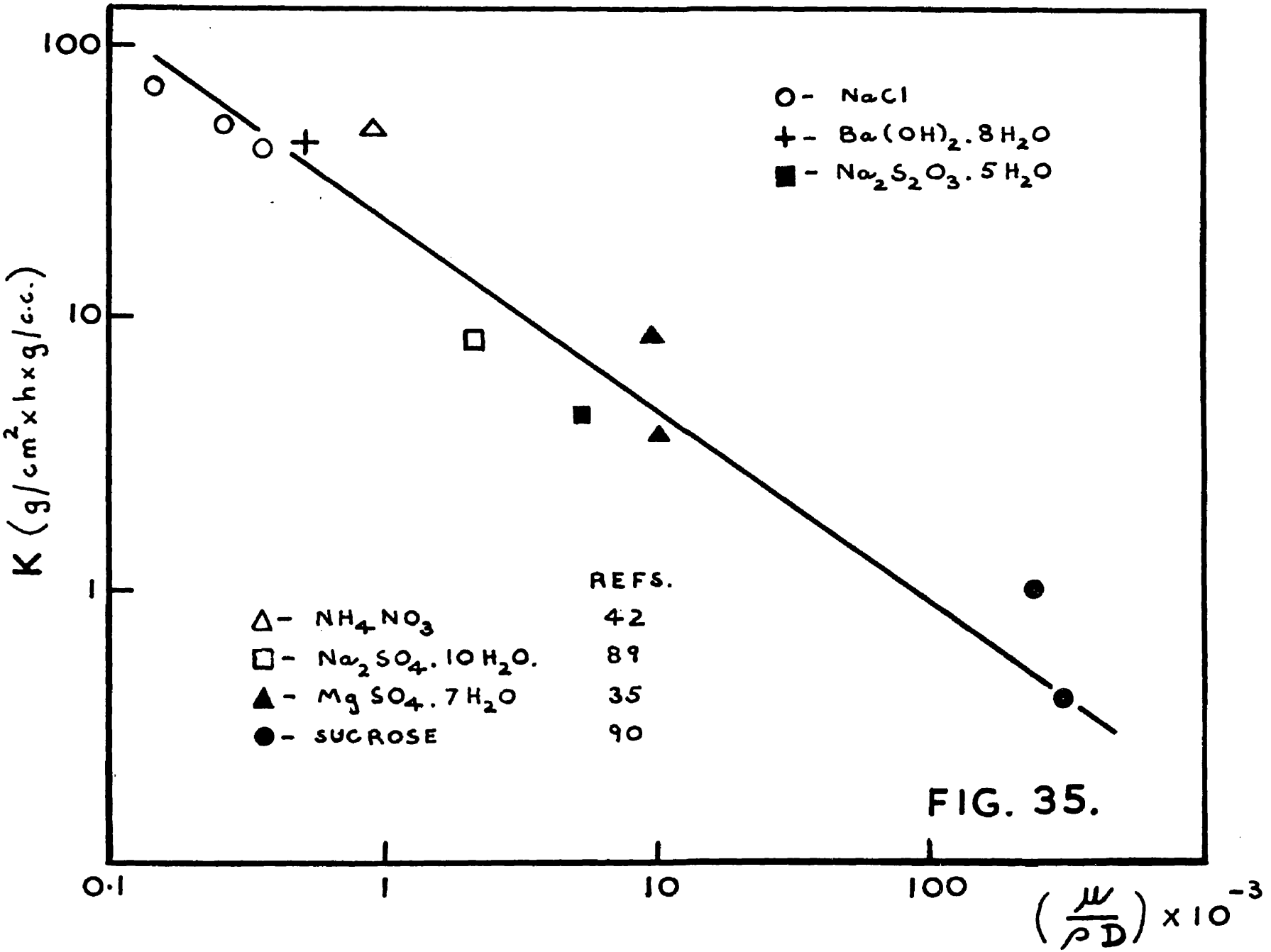

100
10
1
0·1
1
10
100
K (g/cm² x h x g/c.c.)
(μ/ρD) x 10⁻³
O- NaCl
+- Ba(OH)₂.8H₂O
■- Na₂S₂O₃.5H₂O
REFS.
△- NH₄NO₃ 42
□- Na₂SO₄.10H₂O. 89
▲- MgSO₄.7H₂O 35
●- SUCROSE 90

FIG. 35.

have been omitted as too subject to surface control, but the figure shows that there is a possible relationship based on diffusion constants, which can be put in the form

$$K = 22\ Sc^{-0.67}$$

The exponent of 0.67 is the same as that used for diffusive mass transfer from fluidised beds.[77] Unfortunately, diffusion coefficients have never been measured in supersaturated solutions, or even in concentrated solution, and the viscosities of supersaturated solutions are also unknown. If these figures could be determined, and the rates of growth for other solutes determined, then the validity of such a correlation could be more fully tested.

(b) Metastable limit for growth.

A theoretical minimum supersaturation, or metastable limit, for growth has been suggested by Volmer,[47,55] but crystals grow at supersaturation levels which are far below the proposed 50% supersaturation. However, even with a dislocation growth mechanism it is possible that such a metastable limit for growth may exist. Thus, a definite metastable limit for growth was found for sodium chloride crystals at temperatures less than 50°C, the value of the limit varying with temperature. A growth limit was also found

for barium hydrate, but it may have been nucleation on a barium carbonate layer which caused the barrier. The lowest supersaturation measured in hypo crystallisation was 6 gms./litre, and therefore a growth limit is also possible for this solute, since the limits for sodium chloride and barium hydrate were 0.5 and 1.0 gms./litre respectively. Examination of Fig.20 will show that there is a tendency for the growth rate of hypo to decay below 20 gms./litre.

I.C.I. workers[91] have also found a minimum under-saturation necessary for sodium chloride solution, i.e. the curve of growth rate v. supersaturation repeats itself on the solution side with unsaturated solution.

The nature of this barrier to growth must be connected with the formation and development of growth by a dislocation mechanism, which at higher supersaturations is overcome by diffusive presentation of solute. Cabrera and Burton[92] propose such a mechanism, and Fig. 36a shows an ideal growth curve for this mechanism. Neither sodium chloride nor barium hydrate, with or without additives, showed growth curves of this form, but rather that of Fig.36b. It has been suggested by I.C.I. workers[91] that if sodium chloride growth is taken to higher supersaturations then a growth curve is developed similar to Fig.36a,

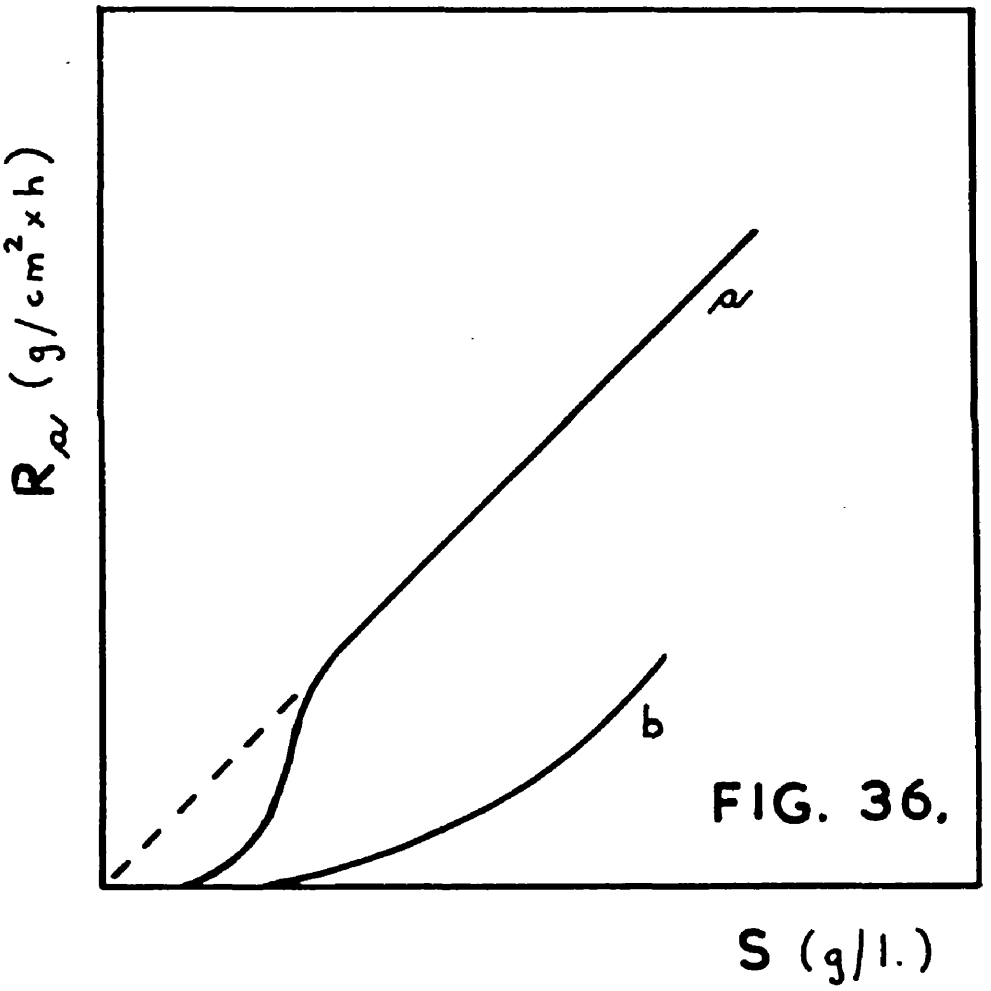


FIG. 36.

and hypo crystals at 24°C (Fig.20) certainly show a growth curve of this form.

(c) Effect of temperature on growth rate.

The rate of growth of sodium chloride crystals was found to increase with temperature, while the rates of growth of hypo and barium hydrate crystals were found to be independent of temperature. Now the factors affecting rate of growth are the rates of surface reaction and diffusive presentation of solute. It is suggested that the rate of surface reaction will resemble a chemical reaction, and will probably show a high temperature coefficient of growth. Any zero temperature coefficient of growth must therefore be explained by some other hypothesis than surface reaction phenomena.

The diffusivity of the solute will be a function of the absolute temperature, the concentration of the solute, and the viscosity of the solution. Increasing temperature will increase the diffusivity; increasing concentration and viscosity will decrease the diffusivity. On the basis of these assumptions the effect of temperature on rate of growth may be considered for each solute.

Sodium chloride shows little increase in concentration with temperature, and a decrease in viscosity with temperature, and therefore the diffusivity

should increase with temperature alone. The rates of growth will be more complicated at low temperatures by the effect of the surface reaction. The experimental results agree with the above, since above 50°C the rate of growth is proportional to the effect of temperature and viscosity on diffusivity.

Hypo has a rate of growth which is constant from 30-40°C, but is reduced at 24°C. The diffusivity should remain constant from 30-40°C, because of the minimum in the viscosity-temperature curve (Fig.25). The effect of increasing concentration will not be too great, since the initial solubility is high, and may well be balanced by the increase in the surface reaction rate, which certainly increases from 24-30°C.

The fact that barium hydrate has a zero temperature coefficient of growth can only be explained by variation in the rates of diffusion with temperature, since the mass transfer coefficient is high enough to suggest a diffusion controlled crystallisation process. The diffusivity will increase and viscosity will decrease with temperature, in solutions of constant composition, but a high temperature coefficient of solubility, with a low solubility at 20°C, will check these changes, because of the rapidly increasing concentration.

The theory of growth rate variation with

temperature must remain hypothetical until experimental measurements are made of diffusivities and viscosities in supersaturated solutions.

(d) The effect of solution velocity on growth rate.

Since a fluidised bed is free to expand with solution flow the effect of solution velocity on growth rate should be small. However, the effect of solution velocity was found to be appreciable. The exponents of the modified Reynold's Numbers in the equation

$$K = B(R_e)^x$$

were 0.13 and 0.25 for sodium chloride and hypo. It is suggested that the small diameter fluidisation tube (1 inch), and the shallow beds used in the experiments combined to produce a wall effect, and it was only at the higher velocities that the bed was freely expanded, with better distribution of fresh supersaturated solution.

However, the variation with velocity is small from an industrial point of view, but is, of course, important theoretically.

(e) Factors effecting scale up of Oslo crystallisers.

Griffiths[73] stated that crystallisation rates are very fickle constants to measure, and unless thorough agitation is used repeatable crystallisation rates are

impossible to achieve. Now it can be seen from the various graphs that the crystal growth rates were reasonably regular and repeatable. Furthermore, since the investigation of sodium chloride was carried out from a batch scale up to a continuous pilot plant scale, and the results were consistent throughout, then it is justifiable to say that a small, batch cooling, fluidised bed crystalliser will give results which are applicable to continuous fluidised bed crystallisers, whether cooling or evaporative models.

Seldom do two investigators find the same value for the growth rate of a specific solute. In a discussion on the effect of agitation on sucrose growth rate Van Hook said[93] " Opinions differ concerning the influence of stirring and agitation upon the crystallisation velocity of sucrose. Experiments on this question have lead different investigators to conclude that there is either a pronounced effect, or relatively none - noncommital decisions being relatively few."

The main reason for variation in investigators results is that there is a big variation in experimental conditions, and therefore the results obtained in the present experiments should only be applied to the design of Oslo crystallisers operating at fluidisation velocities of 3-5 cms./sec.

Any increase in diameter of the suspension

holder will almost certainly cause a different fluidisation pattern, and this may have a marked effect on crystal size and crystal quality. For example, crystals grown in shallow beds in the batch cooling crystalliser showed poor growth structure above 0.07 gms./cm.^{2} x hr.; no poor growth was observed in the crystals from the continuous pilot plant, where crystals growing at the base of the vessel might well have exceeded this rate of 0.07 gms./cm.^{2} x hr. The reason was probably that the system of fluidisation in the deep bed allowed crystals to vary their position greatly, and therefore kept their average growth rate below the critical value.

(f) Continuous crystal production.

A granular crystal product which was above 16 mesh size (> 1 m.m.) was obtained from each of the solutes tested. In terms of sparkle and crystal hardness the quality was always excellent.

If the supersaturation increased beyond the metastable limit then excessive nucleation occurred, but the results of excessive nucleation were different in each case. Sodium chloride produced a myriad of tiny, cubic crystals, which turned the circulating solution to a milky colour. Barium hydrate produced many soft, tiny flakes, while hypo produced relatively few nuclei which grew fairly quickly to a considerable size (0.5 m.m.). By means of a fines separator an

excess of nuclei can be removed, but the increased production caused by high supersaturation is small compared with the added plant complications. A fines separator is only necessary to allow for any fluctuation in operational conditions, or where it is vital to produce large crystals.

The possible production weight is therefore limited by the metastable limit, and the fluidising flow. If the case of sodium chloride is considered, then a production rate of 40 lbs./ft.^{2} x hr. of 2 m.m. crystals was obtained at a metastable limit of 1.6 gms./litre, and a fluidising velocity of 3.2 cms./sec. A fluidising velocity of 6.4 cms./sec. would make possible a production rate of 80 lbs./ft.^{2} x hr., but the bed height would have to be increased to allow for the decreased bed density, and for the increase in crystal surface area necessary to absorb the extra crystalline material. In fact, the bed height would be increased from 3 ft. to 11 ft. A disadvantage caused by increased velocity is that more of the small crystals will be swept round the system, and in general a more rounded product will be obtained because of the increased attrition.

Griffiths[73] proposed an empirical design figure for crystallisers on a crystal production per unit

volume basis. He called this the Separation Intensity Factor, and claimed that all crystallisation operations should be carried out at between 6 and 30 lbs./ft.^{3} x hr. for a 1 m.m. grain product. The experimental results obtained are shown in Table 8, which shows reasonable agreement with Griffiths' range.

Table 8 - Separation Intensity Factors.

Solute	Crystal size m.m.	Production rate lbs./ft.^{3} x hr.	S.I.F. for 1 m.m. grain
sodium chloride	2	13.5	27.0
hypo	6	12.0	72.0
barium hydrate	1.5	6.0	9.0

The comparison between continuous production by cooling or by evaporation was made using two different solutes, sodium chloride and barium hydrate, but they were both of the same type, having a high growth rate and nucleating readily at low supersaturations. It was found to be slightly easier to operate an evaporative plant than a cooling plant. If the metastable limit was exceeded in the evaporative plant then an excess of nuclei was formed, but with little deposition of crystalline material on plant surfaces. The excess nuclei could be removed in a fines separator. Exceeding the metastable limit in a cooling plant brings about blockage of the cooling tubes as well as excessive

nucleation. The cooling plant therefore requires very careful temperature control, and probably a spare cooler. In an evaporative crystalliser small crystals will tend to dissolve on passage through the heat exchanger, while in a cooling crystalliser they will tend to grow on passage through the heat exchanger. Good vacuum and temperature control is, of course, necessary in a vacuum evaporative plant, since a sudden increase in vacuum will produce a shower of nuclei.

Another difference between these forms of working is that the problem of flocculation was met with under cooling conditions, but not under vacuum evaporative conditions. Under vacuum conditions any air circulating with the solution was removed in the flash-head, whereas any air entering under cooling conditions was free to circulate and form stable flocs with small crystals. This mechanism may have been aided in the cooling crystalliser by the alkaline nature of the solution, since such a solution is more prone to form soapy foams than the neutral solutions used in the vacuum crystalliser.

Correlation between laboratory and plant conditions.

The work on continuous crystal production was hampered by lack of time and labour. Since crystallisers take a long time to reach equilibrium conditions,

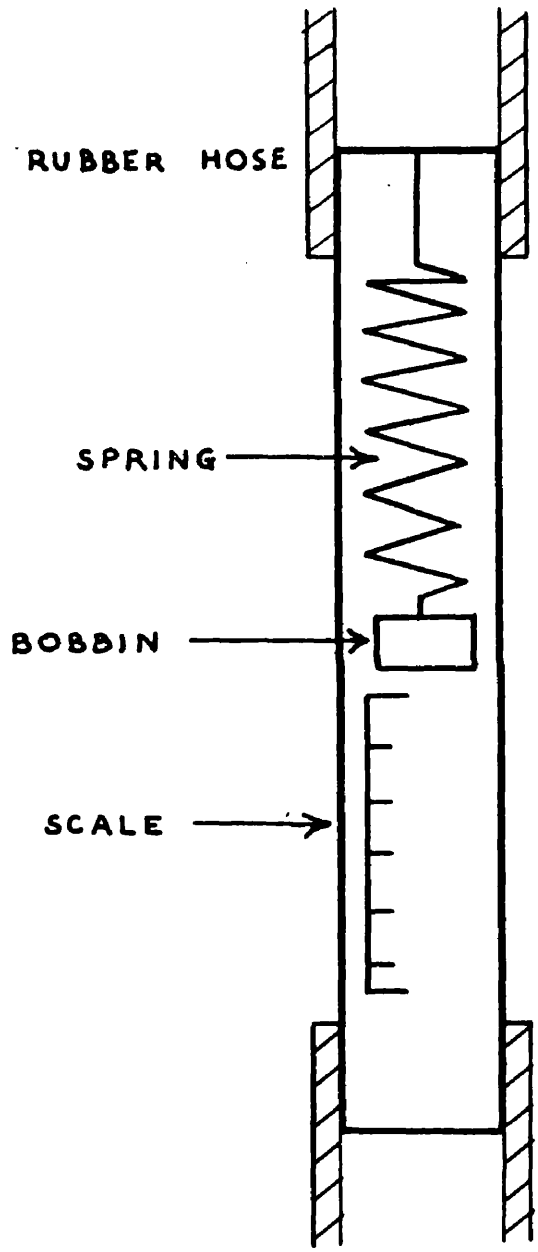
automatic control of temperature and volume of feed, crystallisation temperature and cooling water flow, and rate of product removal is necessary to reach stable conditions. Shift operators are also necessary to prepare feed solution and process further the product crystals. Perhaps the nearest approach in a College laboratory to continuous conditions, with the minimum of supervision, could be achieved by use of a glass laboratory plant, automatically controlled, with a large feed reservoir and a large finished product tank. Product removal could be governed by a slide valve controlled by a photo-electric cell focused on the fluidised bed level. If a deep bed (6 ft.) is used in such a plant, then conditions should approach very closely those of a full scale plant working continuously.

E. Appendices.

(a) A flow meter for hot saturated salt solutions.

In the course of the work on the crystallisation of sodium chloride it became necessary to measure the flow of hot saturated solution passing vertically downwards through a pipe of two inches diameter, at a rate of 25-35 gallons per minute. A conventional rotameter was not readily obtainable, while the orifice plate originally installed, with leads to a gauge, was choked at once with salt deposits. A section of the pipe was replaced by a three foot length of two inch bore glass tubing, in which was hung, by a supporting wire spider, a vertical spring with a wooden bobbin at the end (Fig.37). The spring was of phosphor bronze wire, coiled to a $\frac{3}{4}$ inch diameter, with 12 turns to the inch length, and a total length of 9 inches. The wire was 18 S.W.G. in thickness, and the coil, as constructed, gave an extension of 0.092 cms. per gram of load. The wooden bobbin, in hard wood, was a cylinder of $\frac{3}{4}$ inch diameter and $\frac{1}{2}$ inch long.

The extension of the spring in the tube was calibrated against saturated salt solution at room temperature. The results are shown in Fig.38. Since the spring extension should be proportional to the velocity head, the extension has been plotted against the square of the solution flow in Fig.39 which shows this relation as generally established, though there is



SPRING FLOWMETER

FIG. 37.

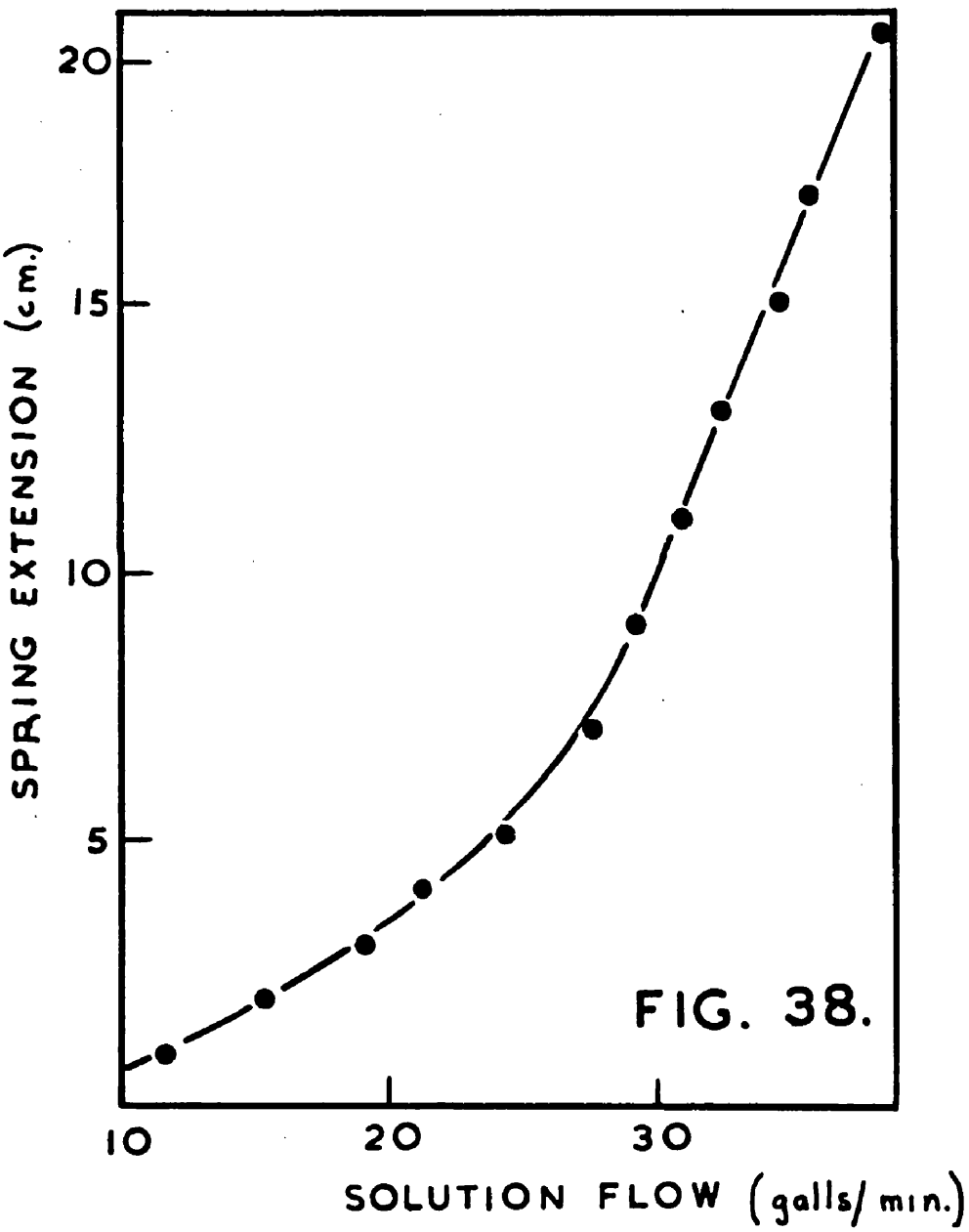

20
15
10
5
SPRING EXTENSION (cm.)
10
20
30
SOLUTION FLOW (galls/min.)

FIG. 38.

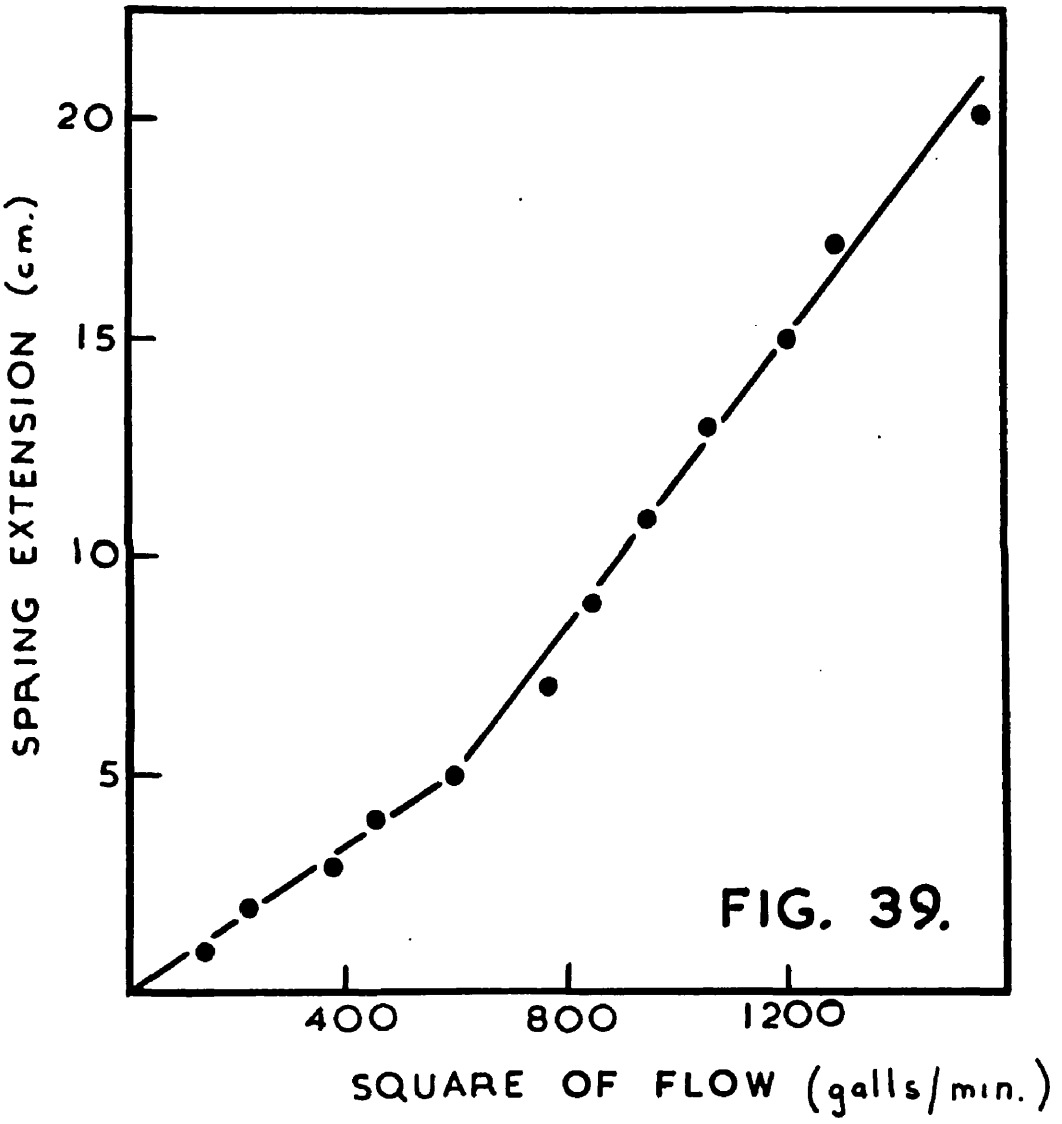

20
15
10
5
SPRING EXTENSION (cm.)
400
800
1200
SQUARE OF FLOW (galls/min.)

FIG. 39.

break in the middle of the graph.

The device was installed in the crystallisation plant, and operated with entire satisfaction for about 12 months of intermittent use. No crystals formed on either spring or bobbin, despite the occurrence of slightly supersaturated conditions, and the presence of fine crystals in the circulating solution. Since then some experimental work has suggested that the device would operate more smoothly in a smaller tube - about 1.5 inches in diameter.

(b) Crystallisation of sucrose.

Sucrose is a very important foodstuff, and it is estimated that 43 million tons are manufactured each year. Perhaps the most important of the manufacturing processes is that of crystallisation where careful control is necessary in order to prepare high purity crystals of the correct size. Crystallisation is carried out in vacuum evaporators with natural circulation, and may be finished in stirred cooling crystallisers. These operations are carried out batchwise under very variable conditions, since at the beginning of a batch only a small amount of seed is present in a large volume of solution, while at the end of the run a large mass of product crystals are present in a small volume of solution.

The surface area therefore varies greatly, and

at the start of the run, when the surface area is small, a small production rate must be adopted to prevent excessive nucleation. However, since the circulation is normally thermal circulation, a small production rate means poor circulation; also at the end of the run when the magma has thickned, the dense, viscous mass prevents easy circulation. Webre[95] suggested that the Oslo crystalliser would produce more constant conditions, and would especially help in the production of large (6 m.m.) preserving crystals, where the available crystal surface area is small and " false grain" is undesirable. No mention has been found in the literature of any experimental work on the crystallisation of sucrose in Oslo crystallisers.

Crystallisation experiments were carried out in the laboratory Oslo crystalliser at 35 and 55°C, and the crystals in the bed grew readily to 6 m.m. crystals at a 100 gms./hr. production rate. It was found that the fluidisation velocity had to be circa 0.5 cms./sec., or large 6 m.m. crystals were swept over to the pump, and blocked the lines. The density of sucrose is 1.59 gms./c.c., and the density of saturated sucrose solution is 1.355 gms./c.c. at 55°C. This very small density difference makes even fluidisation very difficult, and the crystals behave like feathers floating on air currents, any currents of solution

carrying them away to the pump. This was intensified by the heavy syrup causing cavitation at the pump at vacuum greater than 22 ins. of mercury, and by fluctuating pump flow, caused by resistance in the pump gland from carmelised sugar. These practical difficulties might be overcome on a full scale plant because of the greater hydrostatic head, the smaller relative resistance on the gland of a large pump, and the fact that a larger pump and pipelines would not block so readily with large crystals. However, there will always be a tendency to draw large crystals through the system.

Pure saturated sucrose solutions have a viscosity of circa 1 poise, which decreases with increasing temperature, and supersaturation can more than double the viscosity. Impure saturated molasses can have viscosities as high as 200 poises, with normally a minimum viscosity at 50-60°C, and solution viscosity may therefore be an extremely important factor in sucrose crystallisation in industry. Extensive work has been done on the rate of growth of sucrose crystals,[90,96,97] and it has been suggested that above 70°C[38] the crystallisation of sucrose is diffusion controlled. Normal industrial crystallising temperatures are 60-65°C. Therefore any method of increasing the crystal slurry turbulence would be

beneficial.

During high production rates the massecuite velocity through the heating tubes is of the order of 15 cms./sec.[98] The relative velocity of the crystals and solution may therefore be higher than the 1 cm./sec appertaining to the Oslo crystalliser. However, at the end of a batch, the massecuite velocity through the heating tubes drops[99] to 0.3 cms./sec. Therefore, overall, the Oslo crystalliser would probably have as much agitation during production as a natural circulation evaporator, and there would be advantages gained in better nucleation and temperature control i.e. no hydrostatic head causing high boiling temperatures and dissolution of crystals.

Kucharenko[90] studied the rate of sucrose crystal growth, and his results may be recalculated to give a mass transfer coefficient of 0.78 gms./cm.^{2} x hr. x gm./c.c. at 60°C. The metastable limit of sucrose is such that the ratio of supersaturated to saturated concentration is 1.2 before nucleation becomes excessive.[100] At 60°C this represents a supersaturation of 184 gms./litre and therefore a crystal growth rate of 0.144 gms./cm.^{2} x hr. at inlet to the bed. If a concentration drop of 100 gms./litre through the bed is assumed then the production rate will be 375 lbs/hr. at a solution velocity of 0.5 cms./sec. through the

suspension holder. The log. mean supersaturation will be 128 gms./litre, which will produce an average growth rate of 0.1 gms./cm.^{2} x hr. If the bed crystals are assumed to be 6 m.m. in size, then a fluidised bed depth of 12 ft. will be sufficient to remove the deposition concentration. The rate of crystal growth under these conditions is comparable to that of hypo crystals in the proposed full scale crystalliser, and therefore a sucrose crystalliser 4 ft. in diameter and 12 ft. deep should produce 1.8 tons per hour of large sucrose crystals. The crystal size will of course depend on the nucleation rate under these conditions, but the supersaturation ratio of 1.2 is generally accepted as giving a low rate of nucleation.

For the reasons already stated the experimental work was discontinued in the glass plant, and not attempted in the pilot plant because the high temperature coefficient of solubility made continuous work for several days essential, and created problems of handling large volumes of highly viscous syrup with limited equipment and labour.

Appendix C.

Mathematical treatment of crystal size distribution.

The following theory has been abstracted from the work of Saeman.[71]

The relationship between crystal size and volume may be given as

$$l = k_1 v^{\frac{1}{3}} \qquad \text{----------(1)}$$

where k_1 is a constant.

The relationship between growth rate and supersaturation may be given as

$$\frac{dl}{dt} = k_2 S \qquad \text{----------(2)}$$

where k_2 is a constant

or

$$l = k_2 St \qquad \text{----------(3)}$$

Now for classified product removal (i.e. only full sized crystals are removed from the suspension) the number of crystals in suspension smaller than l is equal to the seed rate N, times the age t of crystal, size l,

$$\text{i.e.} \quad Z = Nt = \frac{Nl}{k_2 S} \qquad \text{----------(4)}$$

A similar relation between cumulative crystal weight and size l may be proposed. If dZ is the number of crystals in size increment dl then

$$dW = \frac{l^3 \rho \, dZ}{k_1} \qquad \text{----------(5)}$$

where ρ is the crystal density.

Using the derivative dZ from equation (4)

$$dW = \frac{l^3 \rho N dl}{k_1 k_2 S} \qquad \text{----------(6)}$$

which on integration gives

$$W = \frac{\rho N l^4}{4 k_1 k_2 S} \qquad \text{----------(7)}$$

and therefore the cumulative crystal weight varies as the fourth power of the crystal size.

The actual crystal age may be expressed as a function of the draw down time T, which is the ratio of the weight of suspension W, to the production rate, P, or

$$T = \frac{W}{P} \qquad \text{----------(8)}$$

Now $$P = \frac{\rho N l^3}{k_1}$$

and therefore $$T = \frac{W}{P} = \frac{\rho N l^4 / 4 k_1 k_2 S}{\rho N l^3 / k_1}$$

$$= \frac{l}{4 k_2 S} \qquad \text{----------(9)}$$

and since $l = k_2 S t$

$$T = \frac{t}{4} \qquad \text{----------(10)}$$

Therefore the age of classified product crystals is four times the draw down times.

To facilitate further work it is convenient to replace absolute crystal size l by $\frac{l}{L}$ where

$$L = k_2 S T$$

Thus $$W = \frac{\rho N l^4}{4 k_1 k_2 S} \qquad \text{----------(7)}$$

$$= \frac{\rho N T L^3}{4 k_1} \left(\frac{l}{L}\right)^4 \qquad \text{----------(11)}$$

The function $\left(\frac{l}{L}\right)^4$ is plotted against $\frac{l}{L}$ in Fig.40.

Now the product crystal size for classified removal is 4L, and therefore the total weight of suspension is

$$W = \frac{\rho N T L^3}{4k_1} \left(\frac{4L}{L}\right)^4$$

$$= \frac{64 \rho N T L^3}{4 k_1} \qquad \text{----------(12)}$$

Size distribution for mixed product removal.

In this case product is withdrawn directly from uniformly mixed suspension, and therefore the probability that smaller crystals will be removed as product is proportional to the respective population densities. It follows that there will be more small crystals present in the suspension than will be accounted for by the simple fourth power relation.

It may be assumed that the crystal size range is subdivided into equal size intervals, where n is the

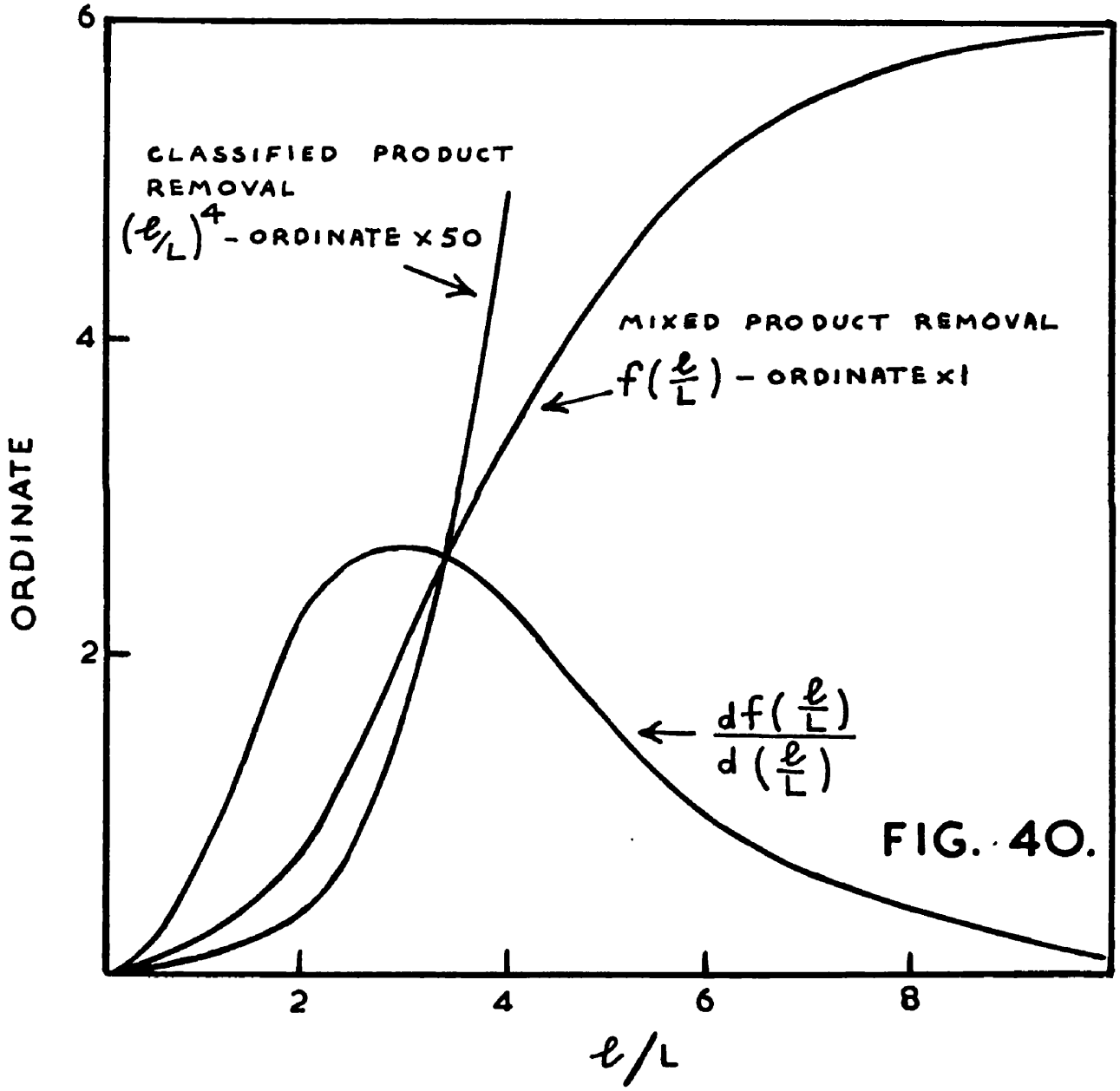

6
4
2
ORDINATE
CLASSIFIED PRODUCT REMOVAL
$(\ell/L)^4$ - ORDINATE x 50
MIXED PRODUCT REMOVAL
$f(\frac{\ell}{L})$ - ORDINATE x 1
$\frac{df(\frac{\ell}{L})}{d(\frac{\ell}{L})}$
2
4
6
8
ℓ/L

FIG. 40.

population density of crystals within the interval. Since the number of crystals withdrawn per unit time is proportional to the population density and the withdrawal rate

$$\frac{dn}{dt} = -\frac{n}{T} \qquad \text{----------(13)}$$

and therefore

$$n = n_o e^{\frac{-t}{T}} \qquad \text{----------(14)}$$

where n_o is the initial population density of seeds.

The value of n_o is equal to the seed rate divided by the rate of growth, or

$$n_o = \frac{N}{k_2 S} \qquad \text{----------(15)}$$

Equation (14) can then be rewritten as

$$n = \frac{NT}{L} e^{\frac{-l}{L}}$$

Now as shown previously the weight of crystals in any size interval is

$$dW = \frac{\rho l^3 \, dZ}{k_1}$$

In this case $dZ = n \, dl$, and so

$$dW = \left(\frac{\rho NT}{k_1 L}\right) l^3 e^{\frac{-l}{L}} dl \qquad \text{---------(17)}$$

which when integrated gives

$$W = C - \left(\frac{\rho N T L^3}{k_1}\right) e^{-\frac{l}{L}} \cdot \left[6 + 6\left(\frac{l}{L}\right) + 3\left(\frac{l}{L}\right)^2 + \left(\frac{l}{L}\right)^3\right] \quad \text{---(18)}$$

and hence

$$W = \left(\frac{\rho N T L^3}{k_1}\right)\left(6 - e^{-\frac{l}{L}}\right) \cdot \left[6 + 6\left(\frac{l}{L}\right) + 3\left(\frac{l}{L}\right)^2 + \left(\frac{l}{L}\right)^3\right] \quad \text{---(19)}$$

The variable term in equation (19) can again be represented as a function of $\left(\frac{l}{L}\right)$

$$f\left(\frac{l}{L}\right) = \left(6 - e^{-\frac{l}{L}}\right)\left[6 + 6\left(\frac{l}{L}\right) + 3\left(\frac{l}{L}\right)^2 + \left(\frac{l}{L}\right)^3\right] \quad \text{------(20)}$$

and is plotted in Fig 40.

Equation (13) also represents the crystal size distribution for crystals withdrawn as product

$$\frac{dP}{dl} = \frac{\rho l^3}{k_1} \frac{dn}{dt} = -\frac{l^3 \rho n}{k_1 T} \quad \text{----------(21)}$$

Substitution of (16) in (21) gives

$$dP = \left(\frac{\rho N}{k_1 L}\right) l^3 e^{-\frac{l}{L}} dl \quad \text{----------(22)}$$

or by analogy with equation (17)

$$P = \rho \frac{N L^3}{k_1} f\left(\frac{l}{L}\right) \quad \text{----------(23)}$$

Now the derivative curve for $f\left(\frac{l}{L}\right)$ with respect to $\left(\frac{l}{L}\right)$ is shown in Fig.40, and it can be seen that mixed product will have a dominant crystal size of $\frac{l}{L} = 3$,

compared with the size $\frac{L}{L} = 4$ found for classified production.

Comparison of seeding requirements for both systems.

Now under equivalent conditions of bed weight and production rate, the draw down time T and crystal reference size L will be the same for both systems.

Then only different seed rates can produce equivalent conditions in both systems.

$$\text{i.e.} \quad W_c = \frac{64\rho N_c T L^3}{k_1} = W_m \qquad \text{----------(24)}$$

$$= \frac{6\rho N_m T L^3}{k_1}$$

$$\text{and} \quad P_c = \frac{64\rho N_c L^3}{k_1} = P_m \qquad \text{----------(25)}$$

$$= \frac{6\rho N_m L^3}{k_1}$$

where subscripts c and m refer to classified and mixed removal of product.

Hence $N_c = 0.094\ N_m$

and therefore under comparable conditions the required seed rate for mixed product is eleven times the number required for classified product.

References.

1. Bennett, R. C. and Newman, H. H., Chem. Eng. Progr., 1959, 55, 65.
2. Miller P. and Saeman, W. C., ibid., 1947, 43, 667.
3. Butler, R. M., University of London Thesis, 1950, " Factors affecting the rate of growth of crystals from aqueous solution."
4. Ostwald, W. Z., physik. Chem., 1900, 34, 493.
5. Miers, H. A. and Miss F. Isaac, J. Chem. Soc., 1906, 89, 413.
6. de Coppet, L. C., Ann. chim. et phys., 1907, 8 ser., 10, 457.
7. Young, S. W.,J. Am. Chem. Soc., 1911, 33, 148.
8. Preckshot, G. W. and Brown, G. G., Ind. Eng. Chem., 1952, 44, 1314.
9. Hulett, G. A., J. Am. Chem. Soc., 1905, 27, 49.
10. Van Hook, A., and Kilmartin, E. J., Electrochem., 1952, 56, 302.
11. Freundlich, H., " Kapillorchemie" , Leipzig, 1909, 144.
12. Knapp, L. F., Trans. Far. Soc., 1922, 17, 457.
13. Van Hook, A., Z. Zuckerind, 1956, 6, 25.
14. Dunning, W. J., " Chemistry of the Solid State" , Butterworth, London,1955.
15. Van Hook, A. and Bruno, A. J., " Crystal Growth" , Disc. of the Far. Soc., No.5, 1949.

16. Van Hook, A. and Frulla, F., Ind. Eng. Chem., 1952, 44, 1305.

17. Dunning, H. J. and Shipman, A. J., Congr. intern. agr. y aliment., 10th Congr., Madrid, 1954.

18. Richards, W. T., Kirkpatrick, E. C., and Hutz, C. E., J. Am. Chem. Soc., 1936, 58, 2243.

19. Kucharenko, Planter Sugar Mfg., 75, 1928.

20. Tammann, G., " States of Aggregation" , Van Nostrand, New York, 1925.

21. Becker, R., and Doring, W., Ann. Phys., 1935, 24, 719.

22. Amsler, Helv. Phys. Acta, 1942, 15, 699.

23. Herquet, L. H., Intern. Sugar J., 1951, 53, 53.

24. Van Hook, A., and Biggins, W. F., ibid, 1952, 54, 7.

25. Van Hook, A., " Principles of Sugar Technology" Elsevier Publishing Co., New York, 1959, Vol.2, p.131.

26. Baker, W. O. and Smyth, C. P., J. Am. Chem. Soc., 1939, 61, 2063.

27. McCabe, W. L., and Ting, H. H., Ind. Eng. Chem., 1934, 26, 1201.

28. Booth, A. H., and Buckley, H. E., Can. J. Chem., 1955, 33, 1162.

29. Noyes, A. A., and Whitney, W. R., Z. physik Chem., 1897, 23, 689.

30. Nernst, W., Z. physik. Chem., 1904, 47, 52.

31. Leblanc, M., and Schmandt, W., ibid, 1911, 77, 614.

32. Marc, R., ibid, 1908, 61, 385; 1909, 67, 470.

33. Van Hook, A., "Principles of Sugar Technology", Vol.2, p.174.

34. Riddiford, A. C., J. Phys. Chem., 1952, 56, 745.

35. Hixson, A. W., and Knox, K. L., Ind. Eng. Chem., 1951, 43, 2144.

36. Buckley, H. E., "Crystal Growth", 1949, p.312.

37. McCabe, W. L. and Stevens, R. P., Chem. Eng. Progr., 1951, 47, 168.

38. Holden, A. N., "Crystal Growth", 1949, p.312.

39. Berthoud, A., J. Chim. phys., 1912, 10, 624.

40. Spandenberg, K., Neues Jahrb. Mineral Geol., 1928, A57, 1197.

41. Humphreys-Owen, S. P. F., "Crystal Growth", 1949, p.144.

42. Jenkins, J. D., J. Am. Chem. Soc., 1925, 47, 903.

43. Wenk, W., Z. Krist., 1910, 47, 124.

44. Van Hook A., Socker Handl., 1953, 8, 45.

45. idem, "Principles of Sugar Technology", Vol.2, p.169.

46. Marc, R., Z. physik. Chem., 1910, 73, 685.

47. Volmer, M., Z. physik. Chem., 1922, 102, 267.

48. Kossel, W., Nachr. Ges. Wiss. Gottingen, 1927, 135.

49. Kaicchew and Stranski, I. N., Z. physik. Chem., 1934, 26, 317.

50. Becker, R., and Doring, W., Ann. Physik, 1934, 23, 317.

51. Frenkel, J., J. Phys., Moscow, 1945, 9, 392.

52. Burton, W. K., Cabrera, N., Frank, F. C., Nature, London, 1949, 163, 398.

53. idem., Phil. Trans., 1951, 243, 299.

54. Kossel, W., " Quantentheorie und Chemie" , Leipzig, 1928.

55. Volmer, M., and Schultz, W., Z. phys. Chem., 1931, 156, 1.

56. Burgers, J. M., Proc. Acad. Sci. Amstd., 1939, 42, 293 and 378.

57. Frank, F. C., " Crystal Growth" , 1949.

58. Mott, N. F., and Nabarro, F. R. N., " The Strength of Solids" , Physical Society, London, 1948, p.1

59. Verma, A. R., " Crystal Growth and Dislocations" , London, 1953.

60. Amelinckx, S., Acta Met., 1954, 2, 849.
Nature, London, 1951, 167, 939.
Phil. Mag., 1952, 43, 562.

61. Forty, A. J., Phil. Mag., 1952, 43, 72.

62. Griffin, L. J., ibid, 1950, 41, 196.

63. Verma, A. R., ibid, 1951, 42, 1005; 1952, 43, 441.

64. Dawson, I. M., and Vand, V., Proc. Roy. Soc., 1951, A206, 555.

65. Booth, A. H., Trans. Far. Soc., 1951, 47, 633.

66. Sears, G. W., J. Chem. Physics, 1958, 29, 1045.

67. Dunn, C. W., and Emmett, H., " Crystal Growth" , 1949, p.118.

68. Bunn, C. W., ibid, p.132.

69. Berg. W. F., Proc. Roy. Soc., 1938, A164, 79.

70. Williams, Miss A. P., Phil. Mag., 1957, 2, 317 and 635.

71. Saeman, W. C., A. I. Chem. E. J., 1956, 2, 107.

72. Robinson, J. N., and Roberts, J. E., Can. J. of Chem. Eng., 1957, 35,

73. Griffiths, H., Trans. Inst. Chem. Eng., 1947, 25.

74. Moelwyn-Hughes, E. A., " Kinetics of Reactions in Solution" , Oxford, 1947.

75. Van Hook, A., Ind. Eng. Chem., 1944, 36, 1042.

76. Wilhelm, R. H., Conklin, L. H., and Sauer, T. C., Ind. Eng. Chem., 1941, 33, 453.

77. Chu, J. C., Kalil, J., and Wetteroth, W. A., Chem. Eng. Progr., 1953, 49, 141.

78. de Lisle, R., Crystallographie, 2nd. Ed., 1783, 1, 379.

79. May, W., and Scott, T., and I.C.I., U.S.P. 2,642,355, 16/6/53.

80. N. V. Koninklyke Nederlandsche Zouterindustrie, B.P. 790,457, 5/6/56.

81. McCartney, E. R., and Alexander, A. G., J. Colloid Sci., 1958, 13, 383.

82. Evans, G. C., and Gerald, C. F., Chem. Eng. Progr., 1953, 49, 135.

83. Kneule, F., and Bogenstatter, G., Chem. Ing. Tech., 1956, 28, 221.

84. Robinson, A. E., " Crystal Growth" , 1949, p.315.

85. Federov, E. S., " The Process of Crystallisation" , Priroda, December, 1915.

86. Anscheles, J. M., Z. Krist., 1936, A95, 150.

87. Evans, U. R., " Metallic Corrosion, Passivity and Protection" , 2nd Ed., E. Arnold, London, 1946.

88. Cartier, R., Pindzola, D., and Bruins, P. F., Ind. Eng. Chem., 1959, 51, 1409.

89. Montillon, G. H., and Badger, W. L., ibid, 1927, 19, 809.

90. Kucharenko, J. A., Planter Sugar Mfr., 1928, 53, No.19; 54, No.4.

91. Rumford, F., and Bain, J., Trans. Inst. Chem. Eng., 1960, 38, 10.

92. Cabrera, N., and Burton, W. K., " Crystal Growth" , 1949, p.40.

93. Van Hook, A., " Principles of Sugar Technology" , Vol.2, p.167.

94. Alewijn, W. F., and Honig, P., ibid, p.318.

95. Webre, A. L., Int. Sug. J., 1936, 38, 379.

96. Alewijn, W. F., and Honig, P., Int. Sug. J., 1931, 33, 595.

97. De Vries, G. H., Chem. Weekblad, 1935, 32, 36; 1947, 6 and 7, 83 and 99.

98. Alewijn, W. F., and Honig, P., "Principles of Sugar Technology" , Vol.2, p.343.

99. Webre, A. L., ibid, p.403.

100. idem, U.S. National Comm. I.C.U.M.S.A., New Orleans, 1953.

Nomenclature.

r - radius of particle or nucleus, cms.

v_m - molecular volume, c.c./gm. mole.

v - volume of a molecule, c.c.

ρ_m - molecular density, gm. moles/c.c.

o - surface area of a gm. mole of particle, $cm.^2$

C - solute concentration, gm./c.c.

C_s - saturation concentration, gm./c.c.

s - excess of solute over the bulk solution value, gm./c.c.

σ - surface tension, dynes/cm.

R - gas constant.

T - absolute temperature, °K.

p - vapour pressure, m.m. Hg.

A - surface area of particle, $cm.^2$

μ - chemical potentional of a molecule, cals.

ΔG - change in free energy, k cals./gm. mole.

$J.$ - nucleation rate, number/sec.

E_η - activation energy for diffusion, k cals./gm. mole.

K - mass transfer coefficient, gms./$cm.^2$ x hr. x gm./c.c.

D - diffusivity, $cm.^2$/sec.

δ - film thickness through which diffusion is taking place, cms.

k_R - surface reaction velocity coefficient, gms./$cm.^2$ x hr. x gm./c.c.

μ - solution viscosity, poises.

a - interlayer spacing - cms.

N - number of nuclei formed per hour.

N_f - number of fine crystals removed per hour.

N_p - number of product crystals removed per hour.

F - weight of fine crystals removed per hour.

P - weight of product crystals removed per hour.

l_f - size of fine crystal, ft.

l_p - size of product crystal, ft.

W - weight of crystals in suspension in fluidised bed, lbs.

T - draw down time, hrs.

R - rate of crystal growth, gms./ gm. x hr.

R_a - rate of crystal growth, gms./cm.^{2} x hr.

S - experimental supersaturation, gms./litre.

V - fluidising velocity, cms./sec.

D_p - crystal equivalent diameter, cms.